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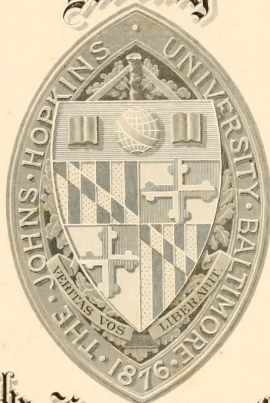


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STUDIES  
in the  
HYDROLYSIS of ACID AMIDES.



DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF

*Johns Hopkins University*

FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

by

*E. Emmet Reid.*

February 1898.

STUDIES

in the

HYDROLYSIS OF ACID AMIDES.

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DISSERTATION

JOHN HOPKINS UNIVERSITY

AND THE DEPARTMENT OF CHEMISTRY

E. KIMMEL, M.D.

BALTIMORE, 1898



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## ACKNOWLEDGMENT.

The author considers it a privilege to express his sincere gratitude to Professor Remsen, at whose suggestion this work was taken up, not only for the regular instruction of the lecture room but more especially for his supervision and guidance of laboratory work. His counsel has ever been timely and valuable, and his kindly interest, an inspiration.

Various analytical difficulties which have arisen during this investigation have caused frequent consultation with Dr. Morse, to whom thanks are now tendered for this as for his earlier laboratory instruction.

Thanks are also due Dr. Renouf for guidance in earlier laboratory work and to Dr. Ames of the Physical laboratory for much valuable instruction.





## Introduction.

Some years ago experiments were carried out in this laboratory, which went to show that an oxidizable group was almost completely protected from oxidation, with chromic acid, when it was in the ortho position with respect to a non-oxidizable group. Later, experiments, not yet published, were tried on the reduction of certain ketohalides, the results going to show that, to a remarkable degree, a nitro group is protected from reduction when there is an other group ortho to it. Still later, remarkable differences were observed in the ease with which benzoyl sulphydrate (saccharin) and formylsulphobenzoyl acid pass into the corresponding acid ammonium salts.<sup>1</sup>

Various experiments had been made by V. H. Meyer and others on the velocity of ester-

<sup>1</sup> J. Amer. Chem. Soc. 41, 1111 (1919).



6  
fication of certain substituted benzoic  
acids and the saponification of their  
esters.

It was thought that possibly the three  
nitrobenzamides might show interesting dif-  
ferences in their rates of decomposition.  
Such differences were found. More than  
that the rates at which the reactions went  
on turned out to be regular and of such  
nature as to permit of a very exact study,  
provided a good method could be found to  
determine with any degree of accuracy the  
amount of decomposition.

The progress and early results of this  
work were reported by Prof. Rosen at a  
meeting of the National Academy of Sciences  
held in New York, Nov. 1, 1916. A preliminary  
note giving the results of series 1 of Traut, and  
some others, entitled "The decomposition of nitrobenzamides", was published.





the American Chemical Journal, April 1897.

About this time an article<sup>2</sup> came to hand, by J. J. Williams, M. J. G. and L. L. Day, on the hydrolysis of the three substituted benzamides, in which was included a study of the three benzamides. His treatment of these amides appears to have been rather severe and their method of analysis a little rough, yet they felt justified in giving results to the hundredths of a percent, though the only duplicate they gave was 2.6% for *o*. They found *o*-benzamide to be "somewhat more stable than the other two" benzamides. Their conclusions are for the most part entirely in line with those reached in this work.

<sup>2</sup> Jour. Chem. Soc. Feb. 1897, P. 229.



# Theoretical Considerations.

If  $A$  and  $B$  are the initial concentrations of acid and alkali and  $B$  that of the amide, after a time,  $t$ , there will have become  $A - x$  and  $B - x$ . If the reaction proceed regularly the velocity at any time should be found on the product of the concentrations at the time.

Then 
$$v = \frac{dx}{dt} = (A - x)(B - x)k$$

in which  $k$  is a constant depending on the nature of the reacting substances, on the temperature, and perhaps on other things.

$\frac{dx}{(A - x)(B - x)} = k dt$ , on integrating becomes

$$\frac{1}{A - B} \log \frac{A - x}{B - x} = kt + C, \text{ Making } x = 0, \frac{1}{A - B} \log \frac{A}{B} = C.$$

Substituting this value for  $C$  in the above.

we get 
$$\frac{1}{A - B} \log \frac{A - x}{B - x} = kt + \frac{1}{A - B} \log \frac{A}{B}$$

Therefore

$$k = \frac{1}{(A - B)t} \left\{ \log \frac{A}{B - x} - \log \frac{A}{B} \right\}$$



If we are dealing by it ... multiply this by 2.3026:

$$\text{Then } k = \frac{2.3026}{(A-B)t} \log \frac{(A-x)B}{(B-x)A}.$$

This has been used by various chemists and is exactly the same as van't Hoff's expression  $k = \frac{2.3026}{C_{\infty} t} \log \frac{C_t(C_1 - C_{\infty})}{C_1(C_t - C_{\infty})}.$

Since  $C_{\infty} = A - B$ ,  $C_1 = A - x$ , while  $C_t - C_{\infty} = A - (A - B) = B$ ,  $C_1 = A$ , and  $C_t - C_{\infty} = A - x - (A - B) = B - x$ .

$$\text{The equation } k t = \frac{1}{A-B} \log \frac{A-x}{B-x}$$

may be written

$$\log \frac{A-x}{B-x} = (A-B)kt$$

$$\frac{B-x}{A-x} = e^{-(A-B)kt} = \left[ e^{-(A-B)k} \right]^t = m^t$$

which readily shows that the rate of reaction

is directly proportional to the concentration of the reactants.









and the tangent to the curve at last coincides with the curve, the curve approaches as its asymptote as  $x$  approaches its limit  $oc$ .

It is interesting to note that for any one value of  $\log d$ , and therefore of  $d$ , there are two real and unequal values of  $x$  theoretically possible, only one of which can, of course, have any chemical significance.

Many chemists are testing the equation  $\log \frac{1}{x} = \log \frac{1}{x_0} + kx$  for the sake of simplicity for 4.13. This may cause for some difficulties in the experiments. Here it exists in the theory. I can see where the reaction is slow, as was true with some of those studied, this would necessitate making  $k$  very large, which might be impossible owing to the slight solubility of one of the substances, or for some other reason undesirable. By making





$A+B$  both small when  $k$  is very small the velocity might be so small that the experiments would take unreasonably long periods of time. There is a worse difficulty, for if  $A+B=C$ ,

then  $\frac{dx}{dt} (A-x)(B-x)k$  becomes  $\frac{dx}{dt} = C(B-x)k + (B-x)^2 k$ .

Even when  $C$  is large towards the end of the reaction the velocity gets very small and difficult to measure; but if  $C$  be 0, the velocity sooner reaches a limit where it can not be measured.

Fair results were obtained with  $A=28$  &  $B$  when  $\frac{27}{25} B$  was used up, then the velocity had about  $\frac{27}{28} \times \frac{1}{25} = \frac{1}{26}$ , nearly, its original value, while with  $A=B$  at 76.5% composition the velocity would have been only  $\frac{1}{25} \times \frac{1}{25} = \frac{1}{625}$  its original value.

In the following experiments, in calculating the value of  $\log \frac{(A-x)B}{(B-x)A}$ ,  $B$  was always made = 1, since  $x$  was most readily calculated in per cents.  $A$  was expressed in corresponding units. This of course, does not alter the value of the function.



## Preparation of Material

For the experiments in Group I ALL, commercial materials were recrystallized until they were considered pure and converted into the corresponding acids. In the other experiments, o-nitrobenzoic acid was prepared partly from o-nitrobenzoyl chloride and partly by oxidizing o-nitrotoluene with potassium permanganate. p-nitrobenzoic acid was made by nitrating benzoic acid. p-nitrobenzoic acid was obtained by oxidizing p-nitrotoluene. For this purpose it was found best to add 200g p-nitrotoluene to 100g conc.  $\text{H}_2\text{SO}_4$  and 100g  $\text{KMnO}_4$  and heat the mixture to 100°C. The mixture is kept



fully ~~containing~~ for forty or fifty hours.  
The residue of p-nitrotoluene may be recovered  
by distilling with steam, but it is  
not worth the trouble. The p-nitrotoluene  
acid is filtered off and washed with  
water. The ~~residue~~ <sup>treated with</sup>  
solution of ammonia ~~is~~. The residue is  
extracted with hydrochloric acid and is  
precipitated for analysis. The  
residue is recovered and 647g of p-nitrotoluene acid  
is obtained. The residue is p-nitro-  
toluene to the potassium salt.

2. Chlorobenzene acid was made by oxidizing  
chlorobenzene with potassium permanganate.  
Some of the chlorobenzene was purified  
and was used by the day market  
for the purpose.

p-Chlorobenzoic acid was made by oxidizing



commercial p. chloroform with chromic acid  
 and a little heat of the mixture.

m. Brombenzoic acid was made by heating benzoic  
 acid, bromine and water in sealed tubes.

The stuff was made in a sealed tube  
 and by heating the mixture in a bath

containing it. It was finally purified by  
 heating at 100°C. with fuming sulphuric

acid and then by heating in a  
 retort to 180°C. After recrystallizing from  
 hot water it seemed pure.

7. p. Brombenzoic acid was obtained by heating  
 p. chlorobenzoic acid with bromine and water.

Under the same conditions it was  
 easy to obtain in any quantity.

8. o. Iodobenzoic acid was obtained by heating  
 o. chlorobenzoic acid with nitric acid.

The stuff was made in a sealed tube  
body and by heating the mixture in a bath





9 m. Iodobenzoic acid was prepared by oxidizing  
methyl iodobenzoate, using, in fact, the  
same method of oxidizing m. methyl benzoate.  
The methyl iodobenzoate was prepared

10 p. Iodobenzoic acid was made by oxidizing  
picric acid, either with potassium  
permanganate or nitric acid. The latter method  
preference, though it is not. The s.p.  
is 101-102°C. was made according to  
Gallmann's directions for making it to  
benzene, using equimolar quantities of  
o.r.p. toluene. The yield of the pure is 101-102°C.  
o.m.r.p. toluene was prepared.  
o. Methoxybenzoic



with potassium for many years. The methyl  
ether of o.cresol, which was made according  
to Altmann's directions, for making  
the methyl ether of p.cresol. 11.

p. Methoxybenzoic acid was prepared by  
the methylation of p.cresol.

p. Methylbenzoic acid was made by oxidizing  
the methyl ether of p.cresol.

### Making Amides.

All the above acids were converted  
into their amides in the following manner:

1. p. Methoxybenzoic acid was heated  
with ammonia in a retort, at  
100°C. for 2 hours.

The same method was used for making  
the amides of p. Methylbenzoic acid, slightly  
increasing the temperature to 120°C. and  
prolonging the time to 3 hours.



the flask vigorously at times. An electric  
sight viewing was necessary to study  
the reaction. When the reaction was  
complete the flask was expanded  
as much as possible by connecting with  
a piston pump. The flask was then placed  
in a vessel of water which was brought  
to boiling and kept there for some time.

When it was thought that the phosphorus  
reaction was about all gotten out of,  
the acid chloride was cooled and dis-  
solved in several volumes of ether. This  
solution was allowed to run, with vigor-  
ous stirring, into a large flask containing  
ice water. <sup>entrained</sup> conc. ammonia until.

The amides thus made were recrystallized  
from ether, usually in the form of  
the free base.

O, m, p. Amidobenzamides were made by reacting



several days solution of the corresponding nitrobenzene, with ammonia and was recrystallized several times.

**o. Hydroxybenzamide** was made by heating oil of wintergreen in sealed tubes with concentrated

**p. Hydroxybenzamide** was made by heating ethylparoxybenzoate in sealed tubes with conc. ammonia water. Some phenol is formed and the yield of the amide is poor.

**c. Ethoxybenzamide** was made by heating ethylparoxybenzoate with conc. ammonia water.

salicylic acid was prepared by heating salicylic acid, oil of wintergreen, ethyl iodide,





and caustic potash in aqueous solution.

The various studies show, in general, to be considerably more soluble than the corresponding acids. The order of solubility is about that of the acids.

p.Chlor- and p. Nitrobenzoic acids are sparingly soluble, while the p. Brom- and p. Iodo- are very slightly soluble even in boiling water.

The melting points of these acids were taken with a thermometer and are given below.

Acid	m.p. (°C)	lit.
p.Chlor-	172. - 173.2	172, 173, 174
p.Nitro-	140 - 140.2	140 - , 142
p.Iodo-	196	198
p.Chlor-	139.9	141



	Boiling	Ref.
p. Chloro	117.5	110
m. Chloro	116.5	110
p. Hydroxy-	116.2	100-110
c. Chloro	115.1	110
m. Chloro	152-152.2 (sublimed) 151	
p. Chloro	210.6-210.8	
c. Hydroxy-	137.4	110
m. Hydroxy-		110
p. Hydroxy-		110
c. Chloro		110
m. Chloro		75, 78-79
p. Chloro	178.3-178.6	175-177
c. Methoxy-	116.5	110-115
p. Methoxy-		152-163
c. Ethoxy-	160	132-135
c. Chloro	137.5	110
m. Chloro	95	
p. Chloro	152.5	151-157



The following are the results of analyzing the various acids by simply distilling with 10g caustic soda. The following are the results of the analysis.

Acid	Weight	No. c.c. of acid	% N	% H	% O
* m. Nitro-	250 mg.	11.48 cc	21.3 mg N	8.42, %	8.41, %
"	"	11.51 cc	21.06 mg. N	8.41	8.41, %
* p. Nitro-	250 mg	10.50 cc.	21.07 mg. N	8.44, %	8.41, %
"	"	10.63 cc.	21.33 mg. N	8.54, %	8.41, %
m. Brom-	226 mg.	7.57 c.c.	18.74 "	6.97, %	20.65, %
p. Brom	301 mg.	10.4	21.00 "	6.97, %	10.65, %
o. Chlor	234 mg.	10.6	21.47 "	9.16, %	10.67, %
p. Chlor	234 mg.	10.60	21.27	9.16, %	10.67, %
m. Iodic	200 mg.	10.41	21.00	10.35, %	10.47, %
p. Iodic	"	10.61	21.08	"	10.47, %

That is, - in the acid groups.



1. It was found that even much colored solutions of *o*-nitrobenzoic acid can be decolorized and made to give a very white solid by washing the same solid with a little potassium permanganate and a few drops of sulphuric acid.

B. 4, 463. Richter. Also Examining, B. 8, 885

2. Gräbe, A. 176 36.

3. Hubner, A. 143 233.

4. Angstein, A. 155, 5.

5. Hubner, A. 144, 131.

6. Jackson and Kolf, Am. 9, 84.

7. Kekulé, B. 2, 1007

8. *o*-Nitrobenzoic acid was diazotized in the directions given for *o*-nitrobenzoic acid by Kekulé, B. 2, 1007.

9. Beran, B. 18 137; Hubner A. 207, 165.

10. Hubner, B. 18 137; Hubner A. 207, 165.





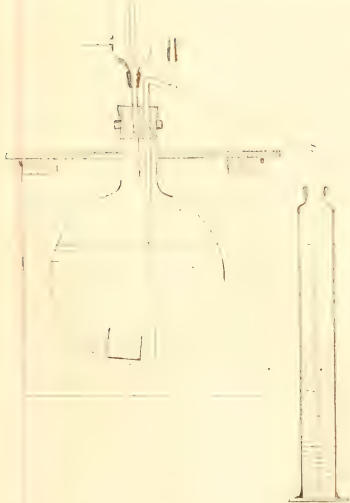




# Experiments. Group I.

Hydrolysis of *o*, *m* & *p*. Nitrobenzamides  
with Hydrochloric & Sulphuric Acids.

Apparatus for Heating Amides  
and Method of Taking Samples.



Eight hundred cubic centimeters of the acid of the desired strength was placed in a one liter flask which was suspended

was kept vigorously

boiling. It was generally kept full by a constant level attachment. Sometimes







was dropped in and the flask shaken for  
 one or two minutes so as to mix the  
 complete solution of the sample. The  
 time was kept by a watch which was  
 always set at a chosen hour exactly, so  
 that the samples always fell due when  
 the hands were in the same position.  
 The time for the falling of the sample was  
 found to be about 1/2 min.

Two flasks were always heated in the  
 same bath. The temperature was  
 put, and into the other flask was  
 the one was put in just five minutes be-  
 fore the other, and exactly the same  
 time was allowed for the falling of the  
 sample.

At the first time the temperature  
 was found to be rising with  
 the upright stand; the time





exit tube being closed until the liquid ceased flowing, when it was opened so as to allow about 1/2 inch in the outer part of the tube to flow out. The amount drawn each time was as near as convenient to 70 c.c. The sample was received in a 250 c.c. cylinder containing 10 c.c. of water. As the way the temperature is immediately reduced to about 40°C., at which the reaction would, at best, go on extremely slowly, and the time required for the reaction to be complete is about 3 seconds.

The operation of taking a sample requires about 3 seconds. After the taking of each sample the outer part of the exit tube was washed out by pouring with distilled water about 10 c.c.

The samples were poured into flasks, the cylinder being washed out twice each



time. These flasks were set aside in regular order and analyzed in the order in which they were taken out.

### Analysis of Samples.

The sample to be analyzed was placed in a flask containing about 100 cc. and washed out twice, the washings being added

to the sample. 10 cc. of a solution containing 5 g. magnesium sulphate to

the 100 cc. solution was added and then caustic soda solution in small fractions until a

slight precipitate of magnesium hydroxide remained after shaking, and finally 2.

to 10 cc. of a solution of the same containing 5 g. NaOH per 100 cc. which was then added to the precipitate and the excess of the magnesium as hydroxide.



The flask was covered by covering it  
 with a cloth and the ammonia distilled off in the  
 usual manner. Steam was furnished  
 it meanwhile to expedite the carrying  
 away of all the ammonia. The flask was  
 removed when the steam had reached to  
 its highest point which was ordinarily  
 about 6 to 8 inches above the flask. When the  
 steam was cut off, to prevent "sucking  
 back". The steam was supplied from  
 fresh containing a little sulphuric  
 acid & potassium bichromate.

The distillate was caught in a  
 small flask. It was  
 a little more standard acid than  
 the first product for the  
 experiment in each case.

This flask was closed by a rubber



stopped carrying a large distillate in  
 and to the bottom of the receiver  
 and was connected to the side of the  
 receiver by a piece of rubber tubing. A  
 smaller tube served to connect <sup>the receiver</sup> with a  
 U-tube of water to be passed for the  
 carbon dioxide of the air. When it was  
 thought that sufficient distillate had  
 been collected the receiver was removed  
 and replaced by a water containing  
 solution. This often showed a trace of  
 ammonia and in most others only minute  
 traces. In some cases an appreciable amount  
 was found and this was neutralized by  
 addition of a drop of dilute acid,  
 which was added to the amount put in  
 the receiver, and the distillation con-  
 tinued until an appreciable amount  
 of ammonia was obtained.





The burner was turned out and the etc  
out of the water. The water was then  
allowed to rise in the condenser and the  
condenser, and 20 c.c. of a solution con-  
taining 0.5% of  $\text{H}_2\text{O}_2$  per c.c. was added  
to the solution by means of a graduated  
vial the amount of  $\text{H}_2\text{O}_2$  solution added.

The strong caustic soda solution hydrolyzes  
the m.p. nitrobenzamide in a very short  
time. The test for nitrobenzamide  
is just as easy to let mine the ammonia  
from these acids as from nitrobenzamide  
itself. The contents of each acid  
was washed out with water which had  
been distilled from acid and then oxidation  
per osmium tetroxide and kept  
in a stoppered wash bottle until you used  
from the carbon dioxide at the end.



The excess of acid was titrated back with standard ammonia solution. The method of titration was as before. The blue ammoniacal indicator was used to give a faint blue color, stirring mechanically, until a blue color appeared, a few drops of indicator was added and the ammonia added a drop at a time to blue color, the readings were taken and the indicator was added until the color changed to blue and again the readings taken. The results given by these two methods were as follows:

Each of the amines in question was added to the solution and the results were as follows:

The results were as follows:



the number of cc. of standard acid neutralized by the ammonia in the two stages, dividing this into the number in the first. Hence the strength of the standard acid used was immaterial, yet it was standardized with care. In the experiments of the series acid methyl was used as an indicator and the above precautions to guard against error were observed, the results being the same.

It was not found practicable to determine o-nitrobenzamide as above, hence in the few experiments where it, a sample was taken in each of 4 runs, and  $\frac{1}{2}$  mols. of a measured amount of the chlorine taken from the mixture after several hours, and the flask



had been used quickly by boiling a stream of solid water. The amount of composition was found by ascertaining the amount of ammonia which is present by distilling as above with the magnesium hydroxide. In this case the number of c.c. of standard acid neutralized was divided by the number of c.c. of standard acid used to determine the amount of the solution taken.

In the following tables are given the results of the analysis of the hydrolyzed form of the acid, along with the amount of acid. The amount of acid, along with the amount of acid, along with the amount of acid.





# Experiments.- Series 1. Nitrogenous

1. 3481 3 0.4147

2. 3482 3 0.4147

1. 1 g. put in flask with 600 cc. of 1.035.4147 N.

Mass	Mass of liquid	Mass of solid	Mass of gas	Mass of liquid
Sample	Weighted	Sample	Weighted	Sample
9.44	1.12	1.12	1.5	1.5
11.2	1.25	1.25	4.0	4.0
1.5	1.33	1.33	1.0	1.0
2.16	1.16	1.16	8.8	8.8

The samples taken for these were those  
 those were not weighed as they  
 were not then thought to contain enough  
 sample. Some of the liquid was  
 made with the rest and found to be  
 good. were not all good, as not enough liquid  
 was caught in the distillations to make some  
 of the ammonia.



Series 2. m. &amp; p. Nitrobenzamidines.

Jan. 20, 1914.

Conc. HCl - A 0.4896 N.

B. conc. conc.

- Amide B 0.04026 N.

B. conc. conc.

Standard  $H_2SO_4$  - 0.1419 N.

The no. cc. of standard acid neutralized in the first distillation is given in column I and represents the amide hydrolyzed, that neutralized in the second distillation, with NaOH,

represents that

m.	I		II		Total		p.		Total	
t	Change	Unchanged	Change	Unchanged	Change	Unchanged	Change	Unchanged	Change	Unchanged
30	5.35	19.95	25.30	26.1	51	5.29	16.41	21.70	2	
60	8.70	16.57	25.27	42.5	68	5.49	9.11	14.60	31.2	
70	9.67	16.5	26.17	50.1	78	13.03	7.26	20.29	36.5	
100	14.39	6.16	20.55	20.0	120	12.69	13.56	26.25	51.25	
100	15.19	3.66	18.85	20.0	120	16.25	2.8	19.05	34.05	
100	18.8	2.2	21.0	20.0	120	19.70	1.3	21.00	31.3	
100	19.67	1.1	20.77	20.0	120	24.01	1.11	25.12	25.6	
100	18.31	1.1	19.41	20.0	120	19.85	2.1	21.95	22.2	

The results given in this table are the results of the







4. HCl conc.  $A = 0.214515$ ,  $B = 0.04026$ ,  $A+B = 0.20465$ ,  $A/B = 6.050$

Feb. 15. 1897.

	$t$	$r$	$T_{\text{obs}}$	$T_{\text{corr}}$	$A - B$	$B$	$\log \frac{(A+B)(A-B)}{(A-B)^2 A + B}$	$\frac{A}{A+B} \times \frac{2.3026}{A-B}$
m.	60	2.11	11.33	11.34	24.6	2.45	15.71	.0167
	100	2.10	11.17	11.17	24.2	2.41	15.69	.0167
	120	2.09	11.06	11.03	23.9	2.38	15.67	.0166
	140	2.07	10.92	10.87	23.4	2.34	15.66	.0165
	160	2.05	10.78	10.71	22.8	2.28	15.64	.0165
	180	2.03	10.64	10.55	22.3	2.23	15.61	.0164
	200	2.01	10.50	10.40	21.8	2.18	15.58	.0163
Exp. Const.	100	16.11	1.76	20.63	82.3	1.14	16.12	.0181
.0181	100	23.10	3.81	17.75	24.5	2.12	16.12	.0181
p.	60	2.18	11.27	11.55	29.5	5.79	10.1	(.0246)
	100	2.17	11.11	11.27	26.2	5.62	10.1	.0241
	140	2.16	10.91	10.91	23.2	5.43	10.1	(.0256)
	180	2.15	10.71	10.71	20.6	5.37	10.1	.0249
	200	2.14	10.51	10.51	17.9	5.30	10.1	.0248
	220	2.13	10.31	10.31	15.3	5.23	10.1	.0247
	240	2.12	10.11	10.11	12.6	5.16	10.1	.0246
Exp. Const.	100	18.11	1.81	18.32	86.8	1.23	18.11	.0220
.0220	100	24.11	2.81	16.10	20.3	1.31	18.11	.0220





S.  $H_2SO_4$  - A - 1.125 N; B - 0.04026; A-B = 1.085;  $\frac{A}{B}$  - 28.02

Standard  $H_2SO_4$  - 0.1411 M

- Hb. 23.10.2

	t	1	2	3	4	5	6	7	8	9
		11.16	13.82	17.92	23.06	27.72	32.4	36.9	41.2	45.2
100	30	6.16	13.82	17.92	23.06	27.72	32.4	36.9	41.2	45.2
	60	7.30	16.28	19.58	24.62	29.28	33.9	38.4	42.9	46.9
	90	10.78	20.53	24.92	30.06	34.72	39.4	43.9	48.4	52.4
	120	13.55	24.8	29.18	34.32	38.98	43.6	48.1	52.6	56.6
	150	15.6	28.1	33.54	38.68	43.34	47.8	52.3	56.8	60.8
	180	17.05	30.97	36.02	41.5	46.16	50.6	55.1	59.6	63.6
A. Cont.	240	19.29	35.6	41.85	47.9	52.56	57.1	61.6	66.1	70.1
0.047	300	20.81	38.31	44.52	50.56	55.22	59.7	64.2	68.7	72.7
	360	22.45	41.11	47.36	53.4	58.06	62.6	67.1	71.6	75.6
	420	24.33	44.0	50.18	56.3	60.96	65.5	70.0	74.5	78.5
	480	26.36	47.03	53.19	59.3	63.96	68.5	73.0	77.5	81.5
	540	28.54	50.13	56.29	62.3	66.96	71.5	76.0	80.5	84.5
	600	30.87	53.3	59.48	65.3	69.96	74.5	79.0	83.5	87.5
	660	33.35	56.6	62.76	68.3	72.96	77.5	82.0	86.5	90.5
	720	35.98	60.0	66.14	71.3	75.96	80.5	85.0	89.5	93.5
	780	38.76	63.5	69.61	74.3	78.96	83.5	88.0	92.5	96.5
	840	41.69	67.1	73.18	77.3	81.96	86.5	91.0	95.5	99.5
	900	44.77	70.8	76.85	80.3	84.96	89.5	94.0	98.5	102.5
	960	47.99	74.6	80.62	83.3	87.96	92.5	97.0	101.5	105.5
	1020	51.35	78.5	84.49	86.3	90.96	95.5	100.0	104.5	108.5
	1080	54.85	82.5	88.46	89.3	93.96	98.5	103.0	107.5	111.5
	1140	58.49	86.6	92.53	92.3	96.96	101.5	106.0	110.5	114.5
	1200	62.27	90.8	96.7	95.3	99.96	104.5	109.0	113.5	117.5
	1260	66.19	95.1	100.97	98.3	102.96	107.5	112.0	116.5	120.5
	1320	70.25	99.5	105.34	101.3	105.96	110.5	115.0	119.5	123.5
	1380	74.45	104.0	109.81	104.3	108.96	113.5	118.0	122.5	126.5
	1440	78.79	108.6	114.38	107.3	111.96	116.5	121.0	125.5	129.5
	1500	83.27	113.3	119.05	110.3	114.96	119.5	124.0	128.5	132.5
	1560	87.89	118.1	123.82	113.3	117.96	122.5	127.0	131.5	135.5
	1620	92.65	123.0	128.69	116.3	120.96	125.5	130.0	134.5	138.5
	1680	97.55	128.0	133.66	119.3	123.96	128.5	133.0	137.5	141.5
	1740	102.59	133.1	138.73	122.3	126.96	131.5	136.0	140.5	144.5
	1800	107.77	138.3	143.9	125.3	129.96	134.5	139.0	143.5	147.5
	1860	113.09	143.6	149.17	128.3	132.96	137.5	142.0	146.5	150.5
	1920	118.55	149.0	154.54	131.3	135.96	140.5	145.0	149.5	153.5
	1980	124.15	154.5	160.01	134.3	138.96	143.5	148.0	152.5	156.5
	2040	129.89	160.1	165.58	137.3	141.96	146.5	151.0	155.5	159.5
	2100	135.77	165.8	171.25	140.3	144.96	149.5	154.0	158.5	162.5
	2160	141.79	171.6	177.02	143.3	147.96	152.5	157.0	161.5	165.5
	2220	147.95	177.5	182.89	146.3	150.96	155.5	160.0	164.5	168.5
	2280	154.25	183.6	188.86	149.3	153.96	158.5	163.0	167.5	171.5
	2340	160.69	189.8	194.93	152.3	156.96	161.5	166.0	170.5	174.5
	2400	167.27	196.1	201.1	155.3	159.96	164.5	169.0	173.5	177.5
	2460	173.99	202.5	207.38	158.3	162.96	167.5	172.0	176.5	180.5
	2520	180.85	209.0	213.75	161.3	165.96	170.5	175.0	179.5	183.5
	2580	187.85	215.6	220.22	164.3	168.96	173.5	178.0	182.5	186.5
	2640	194.99	222.3	226.79	167.3	171.96	176.5	181.0	185.5	189.5
	2700	202.27	229.1	233.46	170.3	174.96	179.5	184.0	188.5	192.5
	2760	209.69	236.0	240.23	173.3	177.96	182.5	187.0	191.5	195.5
	2820	217.25	243.0	247.1	176.3	180.96	185.5	190.0	194.5	198.5
	2880	224.95	250.1	254.08	179.3	183.96	188.5	193.0	197.5	201.5
	2940	232.79	257.3	261.15	182.3	186.96	191.5	196.0	200.5	204.5
	3000	240.77	264.6	268.32	185.3	189.96	194.5	199.0	203.5	207.5
	3060	248.89	272.0	275.59	188.3	192.96	197.5	202.0	206.5	210.5
	3120	257.15	279.5	282.96	191.3	195.96	200.5	205.0	209.5	213.5
	3180	265.55	287.1	290.43	194.3	198.96	203.5	208.0	212.5	216.5
	3240	274.09	294.8	298.0	197.3	201.96	206.5	211.0	215.5	219.5
	3300	282.77	302.6	305.67	200.3	204.96	209.5	214.0	218.5	222.5
	3360	291.59	310.5	313.44	203.3	207.96	212.5	217.0	221.5	225.5
	3420	300.55	318.6	321.31	206.3	210.96	215.5	220.0	224.5	228.5
	3480	309.65	326.8	329.28	209.3	213.96	218.5	223.0	227.5	231.5
	3540	318.89	335.1	337.35	212.3	216.96	221.5	226.0	230.5	234.5
	3600	328.27	343.5	345.52	215.3	219.96	224.5	229.0	233.5	237.5
	3660	337.79	352.0	353.79	218.3	222.96	227.5	232.0	236.5	240.5
	3720	347.45	360.6	362.16	221.3	225.96	230.5	235.0	239.5	243.5
	3780	357.25	369.3	370.63	224.3	228.96	233.5	238.0	242.5	246.5
	3840	367.19	378.1	379.2	227.3	231.96	236.5	241.0	245.5	249.5
	3900	377.27	387.0	387.87	230.3	234.96	239.5	244.0	248.5	252.5
	3960	387.49	396.0	396.64	233.3	237.96	242.5	247.0	251.5	255.5
	4020	397.85	405.1	405.51	236.3	240.96	245.5	250.0	254.5	258.5
	4080	408.35	414.3	414.38	239.3	243.96	248.5	253.0	257.5	261.5
	4140	418.99	423.6	423.45	242.3	246.96	251.5	256.0	260.5	264.5
	4200	429.77	433.0	432.82	245.3	249.96	254.5	259.0	263.5	267.5
	4260	440.69	442.5	442.69	248.3	252.96	257.5	262.0	266.5	270.5
	4320	451.75	452.1	452.66	251.3	255.96	260.5	265.0	269.5	273.5
	4380	462.95	461.6	462.93	254.3	258.96	263.5	268.0	272.5	276.5
	4440	474.29	471.2	473.4	257.3	261.96	266.5	271.0	275.5	279.5
	4500	485.77	480.8	482.81	260.3	264.96	269.5	274.0	278.5	282.5
	4560	497.39	490.5	492.72	263.3	267.96	272.5	277.0	281.5	285.5
	4620	509.15	500.3	502.59	266.3	270.96	275.5	280.0	284.5	288.5
	4680	521.05	510.1	512.86	269.3	273.96	278.5	283.0	287.5	291.5
	4740	533.09	520.0	523.01	272.3	276.96	281.5	286.0	290.5	294.5
	4800	545.27	530.0	533.26	275.3	279.96	284.5	289.0	293.5	297.5
	4860	557.59	540.1	543.61	278.3	282.96	287.5	292.0	296.5	300.5
	4920	570.05	550.3	554.06	281.3	285.96	290.5	295.0	299.5	303.5
	4980	582.65	560.6	564.61	284.3	288.96	293.5	298.0	302.5	306.5
	5040	595.39	571.0	575.26	287.3	291.96	296.5	301.0	305.5	309.5
	5100	608.27	581.5	585.71	290.3	294.96	299.5	304.0	308.5	312.5
	5160	621.29	592.1	596.26	293.3	297.96	302.5	307.0	311.5	315.5
	5220	634.45	602.8	606.91	296.3	300.96	305.5	310.0	314.5	318.5
	5280	647.75	613.6	617.66	299.3	303.96	308.5	313.0	317.5	321.5
	5340	661.19	624.5	628.51	302.3	306.96	311.5	316.0	320.5	324.5
	5400	674.77	635.5	639.46	305.3	309.96	314.5	319.0	323.5	327.5
	5460	688.49	646.6	649.51	308.3	312.96	317.5	322.0	326.5	330.5
	5520	702.35	657.8	659.66	311.3	315.96	320.5	325.0	329.5	333.5
	5580	716.35	669.1	669.91	314.3	318.96	323.5	328.0	332.5	336.5
	5640	730.49	680.5	680.26	317.3	321.96	326.5	331.0	335.5	339.5
	5700	744.77	692.0	690.71	320.3	324.96	329.5	334.0	338.5	342.5
	5760	759.19	703.6	701.26	323.3	327.96	332.5	337.0	341.5	345.5
	5820	773.75	715.3	711.91	326.3	330.96	335.5	340.0	344.5	348.5
	5880	788.45	727.1	723.66	329.3	333.96	338.5	343.0	347.5	351.5
	5940	803.29	739.0	735.51	332.3	336.96	341.5	346.0	350.5	354.5
	6000	818.27	751.0	747.46	335.3	339.96	344.5	349.0	353.5	357.5
	6060	833.39	763.1	759.51	338.3	342.96	347.5	352.0	356.5	360.5
	6120	848.65	775.3	771.66	341.3	345.96	350.5	355.0	359.5	363.5
	6180	864.05	787.6	783.91	344.3	348.96	353.5	358.0	362.5	366.5
	6240	879.59	799.9	796.26	347.3	351.96	356.5	361.0	365.5	369.5
	6300	895.27	812.3	808.71	350.3	354.96	359.5	364.0	368.5	372.5
	6360	911.09	824.8	821.26	353.3					



6.  $H_2SO_4$  A. OBTAINING THE COMPOSITION; A U. S. PAT. 1,167,167

The following table shows the results of the analysis of the product obtained from the reaction of the acid with the metal							The following table shows the results of the analysis of the product obtained from the reaction of the acid with the metal	
	t	t	u	Temp.	Vol.	Pressure	Weight of product	Weight of metal
m.	Cc	3.62	14.37	17.99	25.1	13.73	11.9	.002241
		4.83	15.11	17.87	26.1	13.81	11.8	.002257
		10.11	17.01	18.17	14.1	13.84	11.1	.002337
		The following table shows the results of the analysis of the product obtained from the reaction of the acid with the metal						
	300	14.15	14.1	15.17	15.0	13.11	10.0	.002245
	300	16.46	17.1	17.53	16.3	13.16	11.5	.002257
Av. Comp.	400	15.10	14.1	16.11	14.1	13.11	11.1	.002111
C. 1100	400	31.48	17.13	16.44	11.3	13.10	11.2	.002111
p.	Cc	1.11	14.12	15.13	14.1	13.10	10.1	.002100
	100	11.02	9.1	10.11	10.1	13.11	10.1	.002101
	100	14.00	12.11	11.16	11.1	13.11	11.1	.002111
	100	17.10	14.16	13.11	13.1	13.11	13.1	.002133
	100	19.10	16.11	16.16	16.1	13.11	16.1	.002175
	100	16.11	15.1	15.1	15.1	13.11	15.1	.002160
Av. Comp.	400	16.1	15.1	15.1	15.1	13.11	15.1	.002111
C. 1118	400	17.11	17.1	16.1	16.1	13.11	17.1	.002111



7.  $H_2SO_4$  A 0.0001 N. B. 0.00026 N. A B 0.00006;  $\lambda_B$  2.07

	$t$	$I$	$II$	$III$	$\lambda$	$A$	$\Gamma$	$\frac{A-I}{I-A}$	$\frac{A-II}{I-A}$
m.	60	2.92	15.77	18.71	15.6	691	87.4	.001052	.00987
m. 89.2	120	5.46	12.90	18.20	15.9	677	92.0	.001047	.00978
B. 704.8	180	4.37	11.16	19.23	17.1	657	111.2	.001042	.00961
Temp. 100.35°C.	240	9.93	10.60	20.03	18.1	650	124.7	.001023	.00924
	300	11.01	9.97	20.93	19.1	623	146.1	.001001	.00942
	360	11.20	9.07	19.37	19.7	607	160.2	.000988	.00930
Av. Const.	420	12.17	6.63	18.80	64.7	642	33.3	.000973	.00903
.0093	480	22.38	9.94	32.52	69.4	638	30.6	.000977	.00919
p.	60	3.81	18.65	22.46	17.0	690	83.0	.001162	.0109
m. 110.107	120	5.19	12.77	17.11	17.9	677	101.1	.001144	.01073
B. 782.7	180	8.03	11.61	18.62	18.9	666	117.1	.001133	.01052
Temp. 99.7°C.	240	10.17	10.08	20.17	19.2	667	129.5	.001134	.01046
	300	11.17	8.99	19.63	19.5	650	143.0	.001075	.01035
	360	11.53	6.47	18.10	63.2	613	36.3	.001106	.0104
Av. Const.	420	13.28	3.80	19.08	69.6	637	30.4	.001122	.01035
.0103	480	24.76	7.42	30.32	75.1	633	23.9	.001121	.01035



# Experiments. Group. II.

## Hydrolysis of o, m, & p Nitrobenzamides with Alkalies.

Hydrolysis Apparatus.

The arrangement for carrying out the hydrolysis was carried out in a flask of the same size as above described except that the air which was drawn into the upright tube was made to pass over soda-lime, and a gas inlet was provided for drawing air in the experiments carried out under the boiling temperature. The apparatus for carrying out the reaction is shown in figure 1. The flask is connected to a large thermostat. This consisted of a large container of water. This was heated by a mantle of steam, put in a large specially constructed.





the frequent breaking of the large glass  
 which contained the ~~carcinoma~~ chloride  
 solution, until the glass was replaced  
 by a glass tube about 1/2 inch in diameter  
 and 1/2 inch in length, with a small amount  
 of solution. It was so that as the solution was  
 used the walls and about seven centimeters

in diameter was brought into use and  
 the edge of the bath and was connected with  
 the gas separator by means of a firm rubber  
 joint. Instead of providing a constant  
 supply of gas through the separator, as  
 is usually done, the gas was ap-  
 plied from an independent source, and  
 placed under the other side of the



The tin boiler was covered with thick  
 asbestos board, and was kept fixed to a  
 certain level by being connected through  
 a syphon with a tin vessel containing  
 water. The water in the boiler was  
 one or two degrees of the temperature of the  
 bath of water. The water in the  
 vessel was kept at a constant level by  
 being supplied by a constant flow of water  
 from a tank. The water in the  
 tank was kept at a constant level by  
 being supplied by a constant flow of water  
 from a tank. A considerable difference of temperature  
 could be noted in the various parts of the  
 bath.

When the bath was covered with  
 ordinary calcium chloride solution, the  
 temperature of the bath was set at 50°C.  
 and found to be 50°C. and 50°C. This was  
 found to be the same as the temperature of the

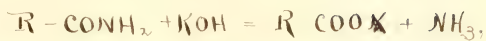






## Analysis of Samples.

Since the reaction



involves the elimination of ammonia which is liable to escape from the alkaline solution, the amount of hydrolysis cannot be determined directly as in the preceding case. The method adopted was to put the sample in the distilling flask with excess potassium hydroxide and to distil off all ammonia until the distillate was no longer alkaline. The acid was then mixed with standard acid connected with the condenser and carried over into the distilling flask to decompose the residual amide and drive over the resulting ammonia. This was titrated in the usual manner. But to determine the per cent. of decom-





position the total amide must be known.

On the same amount of a ~~sample~~ sample put into the same amount of solution, this could be readily calculated from the volume of the ~~sample~~ sample was from as follows.

A 100 c.c. measuring flask was carefully dried and 10.0 c.c. of a solution containing 0.5 g. magnesium sulphate per c.c. or, where the alkali used was barium hydrate, an equivalent amount of magnesium chloride, measured in given bottles. The sample was blown into this in the usual manner. The contents of the measuring solution is immediately rendered turbid by double decomposition with the magnesium salt. The measuring flask was then placed in cold water until it had reached the room temperature, when it was filled up with



water from a burette. The capacity of each measuring flask used was determined by measuring into it the same amount of the magnesium salt solution and filling up to the mark with an alkaline solution of the same strength as that used in the experiments. In this way any error due to the precipitation of the magnesium hydroxide was avoided. To get the volume of each sample it was only necessary to subtract, from this figure, the amount of water required to fill the flask to the mark. The 10.0 c.c., the amount of the magnesium salt solution which had previously been put in. Found in this way the volume of the sample was considered correct to within one cubic centimeter or to about one part in seven hundred, which was accurate enough considering other sources of error.



For convenience in calculating results a table was made out, giving for each <sup>length of a</sup> centimeter of the reacting solution, from 65.0 cc. of 0.88 N. NaOH, the volume of standard acid, 0.1433 N., corresponding to the original content of amide.

The crucibles, flasks and conical side reaction vessels were heated against standard acid using phenolphthalein and methyl orange as indicators, in order to determine the amount of carbonate present. This usually amounted to more than  $1\frac{1}{2}$  of the whole and was disregarded. The crucibles and vessels were then washed free from the acid in water and in other cases a solution of 10% sodium bicarbonate was used. The following tables give the results. In all cases two flasks, the one containing the water and the other the acid, were used in the analysis.



Series I. NaOH A C. 6824A., B- C. 64021-; A B C. 64774;  $\frac{A}{B}$  2.192

*Salmon, W. H. Stan. 14, 56, C. 1, 1/16. M. 1, 10/8/91.*

	$t$	$\pi$ (Unc. ang.)	Yen. Sample	Total C.C. Acid	$\gamma$	$A - x$	$B - x$	$L$ 100 - 98.1	$100 - 98.1$
100.34° C.	30	0.92	81.5	19.51	63.8	1.53	17.4	0.018367	.4477
m.	60	3.24	82.4	23.78	86.1	1.33	13.9	0.010672	.502
	90	1.32	13.2	20.59	93.6	1.25	6.4	0.010377	.509
	120	.63	81.5	23.31	97.3	1.21	2.7	0.010948	.523
	150	.37	81.1	23.12	98.4	1.20	1.6	0.010248	.489
	180	.23	73.3	20.92	98.4	1.20	1.1	0.009434	.462

Ac. Const.	210	13.7	} used through to combine with the ammonia for analysis
0.496	246	19.9	

0.496	246	19.9	) ammonia for analysis
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30	46.2	11.20	11.46	73.1	1 16.1	26.4	.013135	.621
60	1.34	43.70	12.46	89.2	1 30.0	10.8	.012328	.590
90	1.07	19.4	22.55	43.3	1 23.9	4.7	.012001	.576
120	.51	73.0	20.52	97.5	1 21.1	2.5	.011220	.538
150	.28	70.7	20.15	98.6	1 20.6	1.4	.010629	.509
180	.15	64.6	19.55	94.2	1 20.0	.8	.010196	.489

Av. Const.	210	10.8	} Were thought to contain too little ammonia for analysis.
C. 555	240	84.4	

0.555	2.40	84.4	Ammonia for analysis.
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2. NaOH B C.C1846N, A C.C4026N; A B C.C2130;  $\frac{A}{B} = 2.123$

Standard  $H_2SO_4$  C.1477N.

March 30, 1896.

	t	" Exchanged Sample	Vol. of Sample	Sp. of Sample	f λ	A x	B x	log (A x) B log B A x	log 2.802 A, T.
m.	20	13.30	14.5	15.30 8.62	37.8	1.773	63.2	.003400	.584
	40	16.10	12.9	16.10 9.97	47.0	1.633	53.0	.004176	.452
	60	15.43	14.0	16.19 9.84	56.2	1.561	43.8	.003750	.403
	80	15.54	14.5	16.62 22.66	66.0	1.463	34.0	.003788	.410
	100	15.30	81.0	10.82 23.09	10.9	1.414	29.1	.003596	.389
	120	13.23	13.0	9.73 20.80	11.1	1.336	23.3	.003650	.393
	140	13.64	77.2	10.31 22.00	14.9	1.324	20.1	.003512	.379
	160	<del>9.18</del>	51.7	6.91 14.73	19.5	1.325	20.5	sample too small	
p.	20	13.97	67.0	8.93 19.07	37.0	1.783	66.0	.005233	.565
	40	16.06	16.1	10.17 21.69	54.7	1.579	45.6	.005312	.514
	60	13.50	68.4	9.14 19.49	64.7	1.476	35.3	.004923	.532
	80	13.18	76.1	10.14 21.60	12.9	1.394	22.1	.004804	.507
	100	11.37	71.6	9.57 20.41	80.4	1.314	14.1	.005106	.552
	120	12.88	72.9	9.67 20.63	82.8	1.285	14.2	.004582	.495
Ar. Const.	140	11.20	65.4	8.80 18.78	83.2	1.221	11.5	.004335	.468
C. 531	160	13.02	79.0	10.35 22.31	89.0	1.233	11.0	.005162	.558

Percent calculated on alkali used up.



3. NaOH A 0.0491; B 0.0402; A/B 0.02411;  $\frac{A}{B}$  1.61%.

Standard HCl = 0.1433N.

Calc. 1.1.1.

	t	Wt. of Sample	Vol. of Sample	% X	A x	B x	$\log \frac{(A \times B)}{(B \times A)}$	$\frac{0.02411}{A \times B}$	
m.	30	11.96	12.1	20.39	41.1	12.00	58.6	.003446	.321
90.0°C.	60	1.35	66.5	18.63	66.1	100.1	39.3	.003346	.312
	70	5.00	63.1	11.13	71.5	89.6	25.2	.003256	.304
	120	4.52	72.2	20.25	16.2	55.2	23.5	.002883	(.268)
	150	2.88	61.3	18.91	84.8	76.6	15.2	.003297	.307
	180	2.20	64.2	18.03	87.8	73.6	12.2	.003181	.296
	210	1.94	76.1	21.35	90.4	106	9.2	.003224	.300
	240	1.18	84.0	23.60	92.9	65.5	7.1	.003235	.301
p.	25	10.63	65.7	18.46	42.4	119.0	57.6	.004289	.400
	60	5.89	63.2	17.76	66.5	94.6	33.2	.004214	.392
	90	4.46	11.4	20.20	77.9	83.5	22.1	.004104	.382
	120	3.28	14.0	20.79	84.2	77.2	15.8	.004009	.374
	150	2.56	81.6	22.92	88.8	72.6	11.2	.004025	.375
	180	1.65	70.4	19.75	91.1	69.7	8.3	.003979	.371
	210	1.05	58.9	16.53	93.1	61.7	6.3	.003921	.365
	240	.32	22.2	6.24	94.9	66.5	5.1	.003781	.352



4. NaOH A 0.06734 N; B 0.04026 N; A B 0.02708 N;  $\frac{A}{B}$  1.616

Standard HCl 0.1433 N.

Allyl 4.1526

	$l$	Vol. of HCl Sample	Req. Sample	% X	A x	B x	$\log \frac{(A-x)B}{(B-x)A}$	$\frac{dX}{A-B}$	
m.	30	14.03	67.8	19.04	26.2	1408	73.8	.001261	(.105)
80.03°C.	60	14.35	52.5	23.35	38.3	1231	61.7	.001609	.140
Av. 70	90	4.35	78.7	22.11	51.6	1094	42.4	.002094	.114
Boiling pt.	120	6.37	64.2	19.44	67.4	996	32.6	.002136	.236
100° Boiling	150	5.08	68.1	18.27	72.2	948	27.8	.002067	.176
0.12°C.	180	4.28	69.3	19.52	78.1	887	21.9	.002143	.132
Av. Const.	210	3.69	73.0	20.50	82.0	830	17.0	.002268	.193
0.184	240	3.23	78.6	22.08	83.4	816	14.6	.002186	.187
fu.	30	12.41	10.8	19.15	34.6	1324	65.4	.002786	.237
Av. Const.	60	9.26	70.0	19.66	52.9	1141	47.1	.002692	.229
fu. 70	90	5.10	57.7	16.41	64.8	1022	35.2	.002664	.227
0.16°C.	120	4.42	57.0	16.01	72.4	946	27.6	.002602	.221
	150	3.69	62.9	17.67	79.1	829	20.9	.002674	.227
	180	3.71	77.8	21.86	83.0	840	17.0	.002617	.223
Av. Const.	210	2.71	66.3	18.63	85.4	816	14.6	.002500	.213
0.223	240	2.38	82.5	23.33	87.8	792	12.2	.002437	.269



5.  $\text{NaOH}$  A 0.01734; B 0.01064; A-B = 0.00670  $\frac{A}{B}$  1.110

Standard HCl 0.17334

May 1.159%

	t	Vol. of NaOH	Emp. of NaOH	% NaOH	% NaOH	% NaOH	% NaOH	% NaOH	% NaOH
70.07°C.									
	30	15.78	80.8	22.7	17.3	15.7	32.7	.001218	.1097
34 Readings	60	12.21	67.1	15.5	25.1	11.3	11.3	.001127	.1040
Maximum Var.	90	11.14	75.6	21.24	43.5	12.2	36.2	.001362	.108
0.08°C.	120	5.81	63.0	15.25	37.4	12.06	48.6	.001327	.106
	150	5.61	74.5	20.43	38.5	113.5	41.5	.001343	.107
	180	7.27	71.0	14.95	63.6	108.4	36.4	.001324	.105
Av. Const.	210	6.12	65.1	11.13	65.0	104.2	32.0	.001314	.105
0.101	240	5.33	65.7	15.36	71.4	102	28.1	.001301	.101
$\mu$	30	13.55	69.6	17.55	12.8	159.2	87.2	.000863	.0671
NaOH made	60	11.73	67.5	15.76	28.1	142.7	71.9	.001097	.0871
from $\text{Na}_2\text{SO}_4$	90	11.12	72.8	20.75	45.6	126.4	54.4	.001451	.115
and $\text{Ba(OH)}_2$	120	8.34	61.3	17.22	53.7	111.1	46.1	.001442	.112
	150	7.23	42.4	11.41	60.3	111.7	39.7	.001425	.113
	180	5.76	62.5	17.56	66.6	105.7	33.4	.001464	.116
Av. Const.	210	5.15	61.4	17.25	69.1	102.7	35.9	.001366	.109
0.114	240	5.33	74.8	21.02	74.6	107.1	26.4	.001207	.115





6.  $\text{NaOH}$  A 0.06798 N. B 0.04026 N; 4 D - 0.02777.  $\frac{A}{B} = 1.6$

5% 95°C	Handbook AC 0.1-3.2				Handbook AC 0.1-3.2				Handbook AC 0.1-3.2	
	t	Wt. of Sample	Wt. of Sample	Wt. of Sample	t	Wt. of Sample	Wt. of Sample	Wt. of Sample	Wt. of Sample	Wt. of Sample
m.	30	1.1	54.3	15.34	10.1	1.33	82.3	.000690	.0573	
Acid	6	1.31	12.1	20.43	20.1	1.43	14.6	.000719	.0371	
Acid	40	1.36	63.4	14.23	27.9	1.43	12.1	.000707	.0386	
Acid	120	1.4	86.6	22.67	34.1	1.44	13.4	.000693	.0376	
0.25°C.	130	11.66	64.2	14.4	40.1	1.23	11.1	.000697	.0379	
	150	11.55	77.8	21.35	48.8	1.23	10.2	.000710	.0396	
Al. Cont.	210	11.48	81.2	22.31	49.1	1.14	10.3	.000700	.0351	
0.0584.	240	11.36	83.8	22.54	53.8	1.16	10.2	.000713	.0334	
Benzamide	20	13.61	51.4	16.12	3.4	1.65	96.6	.000216		
Acid	6	14.77	24.5	20.33	4.0	1.63	96.0	.000122		
from NaOH	90	11.85	66.6	14.11	4.6	1.62	95.4	.000144		
and 73.04%	120	13.64	71.6	20.11	1.1	1.61	92.4	.000111		
	150	11.37	75.3	21.15	3.4	1.61	91.6	.000116		
	180	16.23	16.7	21.41	1.1	1.61	not comp.			
	210	11.26	13.2	20.56	11.2	1.56	88.3	.000104		
	240	22.02	40.6	25.45	13.4	1.55	86.6	.000152		



7.  $\text{NaOH}$  A 0.0198 N; B 0.0402 N; A-B 0.0212 N;  $\frac{A}{B}$  1.688

Standard  $\text{NaCl}$  0.1233 N

May 25, 1896

	1	Vol. of unchanged sample	Eqv. of sample	$\lambda$	A-x	B-x	$\log \frac{A}{B}$	$\log \frac{2.3026}{A-B}$
m.	30	3.11	62.1	38.1	113.1	14.3	.003990	.599
	60	3.11	62.1					
C. cont.	90	3.65	73.4	83.1	83.1	14.9	.003812	.582
0.484	120	1.53	65.5	74.4	78.4	14.6	.003707	.577
$\mu$ .	30	1.16	64.1	15.23	66.1	108.1	.007072	.587
	60	3.64	65.1	15.27	74.3	89.0	.006944	.576
1. cont.	90	2.11	63.9	11.93	88.2	80.6	.006768	.562
0.572	120	1.12	58.3	24.30	93.1	75.1	.006114	.562

$\text{NaOH}$  made from  $\text{Na}_2\text{S}_2\text{O}_4$  15.1112

Temperature of boiling water



S. KOH A = 0.00138 N; B = 0.00161 N; A/B = 0.02111;  $\frac{A}{B}$  = 1.02

90° C.	t	Standard HCl - 0.1233 N				May 28, 1892			
		Vol. of Hemmings	Sample	Figures	X	A X	B X	Log (A-B) 1 10 2	Log 2.3025 4-B.
m	30	12.04	11.1	16.41	37.1	122.6	60.3	.003401	.289
90.03	61	8.02	13.7	20.69	61.1	106.5	38.4	.003394	.301
40.579	90	3.20	66.7	18.75	12.3	95.0	27.7	.003467	.245
Hemmings	120	4.13	14.1	20.82	80.2	81.1	19.3	.003498	.297
M. S. v.	130	3.28	18.5	22.05	85.1	82.2	14.7	.003458	.293
42.9° C.	180	2.30	73.2	20.58	88.5	18.3	11.5	.003402	.287
Ar. Const.	1	1.14	76.7	11.55	76.0	16.3	9.0	.003336	.286
0.291	4	1.52	76.6	21.52	72.5	15.3	1.5	.003285	.276
p.	3	11.66	11.7	20.20	47.3	120.0	52.7	.004401	.377
	6	6.56	12.3	20.31	67.1	79.6	36.2	.004426	.376
KOH from	7	4.58	14.3	20.57	78.1	87.2	24.1	.004443	.380
K <sub>2</sub> Si <sub>2</sub> and	110	1.12	16.8	21.07	85.2	82.1	17.3	.004338	.365
B <sub>2</sub> (OH) <sub>2</sub> .	130	2.57	74.0	22.17	88.6	78.7	11.4	.004104	.348
	130	1.77	16.3	21.33	91.1	75.6	8.3	.004088	.347
Ar. Const.	12	1.12	62.8	11.67	83.7	73.6	6.3	.004020	.341
0.357	40	.78	87.4	16.12	95.2	72.1	2.8	.003992	.337



9.  $KOH = A = 0.06947N$ ;  $B = 0.04026N$ ;  $A/B = 0.02421$ ;  $\frac{1}{B} = 1.18$

Standard  $HCl = 0.1433$

Temp. 2.184%

50°C.	t	Unchanged	Vol. of Sample	Equival. Sample	% $\chi$	$\chi$	$\chi^2$	$\frac{\chi^2}{\chi}$	$\frac{1}{\chi}$
m.	30	14.33	72.4	20.34	29.5	1.460	70.5	.002646	.209
	60	10.31	10.4	11.13	47.7	1.248	32.3	.002349	.185
79.97°C.	90	7.98	68.8	19.33	58.7	1.138	41.3	.002260	.178
Ans. of 50	120	6.57	71.4	20.06	67.2	1.063	32.8	.002248	.177
Readings.	150	5.08	70.8	19.89	74.5	.980	25.5	.002319	.183
Ans. of 50	180	4.46	74.6	20.20	78.7	.938	21.3	.002261	.178
Ans. of 50	210	3.1	74.5	20.93	81.8	.907	18.2	.002194	.173
C.1.1	240	2.70	64.1	18.01	85.2	.873	15.0	.002205	.174
p.	30	12.35	64.7	17.58	34.2	1.352	65.8	.002550	.225
	60	11.17	85.8	14.12	53.1	1.195	46.3	.002874	.226
NCH made	90	7.02	70.8	19.89	64.7	1.075	35.3	.002760	.217
Ans. of 50	120	5.13	61.5	17.25	72.6	.971	27.4	.002707	.214
(1.130H)	150	4.01	66.5	18.65	78.5	.940	21.5	.002693	.212
	180	3.65	71.1	21.38	82.7	.916	17.1	.002681	.211
Ans. of 50	210		71	20.21	Sample				
C.216	240	1.91	63.1	17.15	84.4	.91	14.0	.002222	.214





10.  $Ba(ClH)_2 = A = 0.06659 N; B = 0.04026 N; A-B = 0.02633 N; \frac{A}{B} = 1.654$

Standard NCI = 0.143316									
June 7, 1896									
91°C.	1	Time used	Sample	Sample	X	A-X	B-X	$\log \frac{A-X}{B-X}$	$\log \frac{A}{B}$
	30	11.61	11.7	14.64	46.1	124.6	44.1	.004907	.365
	60	1.87	11.7	23.05	66.1	94.4	34.8	.004113	.360
45 Readings	90	4.77	72.0	20.22	76.4	84.6	23.6	.011777	.348
Vac. dist.	100	3.76	78.5	22.15	83.0	82.4	17.0	.003882	.340
0.292	150	2.68	75.8	21.30	87.4	11.5	12.1	.003420	.343
	180	1.77	74.3	20.87	90.6	74.8	4.4	.003770	.331
4.5 Const.	210	1.47	73.7	20.71	92.8	72.6	1.1	.003764	.227
0.36	240	.87	59.4	16.73	94.3	70.6	3.2	.003577	.333
	30	16.81	18.3	22.00	50.4	114.5	49.1	.004973	.435
	60	3.87	73.3	20.67	71.5	93.7	26.5	.004986	.436
	90	4.00	73.1	20.83	80.5	84.9	19.5	.004670	.408
	120	2.54	68.7	19.30	87.4	78.5	12.1	.004775	.417
	150	2.13	77.8	21.86	90.7	74.7	7.0	.004576	.400
	180	1.76	75.8	21.30	93.7	71.7	6.3	.004650	.407
4.5 Const.	210	.75	65.7	18.46	95.0	70.4	3.0	.004427	.357
0.409	240	.74	74.3	22.77	76.7	67.0	3.0	.004460	.357



11.  $B_2(OH)_2$  A 0.06712 A.; B 0.04026 A.; A B 0.01786,  $\frac{A}{B}$  1.012.

Temp. 25°C. = 77°F.		Temp. 25°C. = 77°F.		Temp. 25°C. = 77°F.		Temp. 25°C. = 77°F.		Temp. 25°C. = 77°F.	
S.C.C.	t	Hand. gpt. Sample	Impurity Sample	$\lambda$	A- $\lambda$	Hand. gpt. Sample	Impurity Sample	$\lambda$	A- $\lambda$
68 Readings	30	11.00	71.8	21.2	32.5	11.81	67.5	.002582	.216
	60	11.02	72.9	21.3	30.8	117.4	47.2	.002543	.214
	90	8.02	74.9	21.0	61.1	106.3	31.1	.002453	.265
	Max. Ym. 0.18°C.	120	6.41	77.8	21.0	72.5	28.2	.002467	.207
	150	4.12	68.1	11.13	73.5	92.4	14.2	.002371	.199
	180	3.77	92.7	20.45	80.1	88.1	17.4	.002315	.196
Av. Count.	210	3.03	63.2	15.42	84.0	84.2	16.0	.002337	.198
0.204	240	2.65	71.6	20.11	86.8	81.2	13.2	.002321	.177
	30	13.02	13.1	80.9	36.1	112.5	12.3	.003056	.257
	60	11.15	16.5	14.9	57.4	110.5	41.6	.003155	.264
	90	10.1	14.4	22.33	68.2	100.0	31.8	.003019	.283
	120	4.66	12.3	20.31	71.1	91.1	22.9	.003114	.261
	150	3.76	11.1	18.67	80.1	87.3	19.1	.002894	.242
	180	3.06	73.8	20.73	84.2	83.0	14.8	.002905	.243
Av. Count.	210	2.10	12.5	11.66	88.0	80.2	12.0	.002853	.239
0.250	240	2.07	12.3	11.71	76.0	77.6	9.4	.002879	.241



Experiments on o-Nitrobenzamide with Caustic Soda  
at about  $100^{\circ}\text{C}$ .



It was found impossible to distill off the o-nitrobenzamide by distilling off the ammonia from it with caustic soda, as was done with the meta and para nitrobenzamides. This rendered it necessary to collect all the ammonia liberated by the caustic soda during the reaction. To accomplish this the following method was used. 350 mg. o-nitrobenzamide was weighed into a small Erlenmeyer flask and 20 c.c. of the caustic soda solution measured in. The flask was closed by a rubber stopper carrying a tube some 30 cm. long, bent over at the top and passing through the stopper of a T-tube containing more than enough acid to neutralize the



amount of alkali in the flask. The flask was plunged into boiling water and shaken so as to assume the required temperature as quickly as possible.

At the proper time the flask was removed and shaken in cold water to stop the reaction. By tilting the flask when this was done it could be made to suck back much of the acid in the  $V. C.$

The contents of the flask and of the  $V. C.$  together with the washings of both were placed in a distillation flask and after neutralization the magnesium hypochlorite mixture added and the ammonia distilled off in the usual way. The number of cubic centimeters of standard acid neutralized was divided by the volume of standard acid equivalent to 0.5 mg. of nitrogen, and then the factor





The following table gives the results of a series of four experiments with sodium nitrobenzamide in this way. The four experiments were carried out together in the same water bath and the temperature considered to be  $100^{\circ}\text{C}$ .

c. Nitrobenzamide

$\text{NaOH} = A = 0.06734 \text{ N}$ ,  $B = 0.04026 \text{ N}$ ,  $A - B = 0.02708$ ,  $\frac{A}{B} = 1.670$

Amount of Nitrobenzamide					Weight of Ba			
t	Changed	Wt. of Amide	Eq. of Amide	at "	A	B	$\log \frac{A - x}{B - x}$	$\log \frac{2.3025}{A - B}$
a.	60	1.98	300 mg	21.01	8.1	169.0	91.7	
	125	4.21	"	"	20.0	147.0	50.0	
Ar. Co.	185	5.37	"	"	25.3	171.7	76.7	
	245	6.03	"	"	25.6	138.4	14.4	

$\text{NaOH}$  made from  $\text{Na}_2\text{SO}_3$  and  $\text{Ba(OH)}_2$



## Experiments. Group III.

Hydrolysis of various Amides with Hydrochloric Acid.

o, m, and p. Nitrobenzamides,

o, m and p. Amidobenzamides,

o. and p. Chlorbenzamides,

m, and p. Brombenzamides,

o. Iodobenzamide,

o. m, and p. Toluic amides,

o. and p. Hydroxybenzamides,

o. Methoxybenzamide,

o. Ethoxybenzamide,

Method of Tasting Samples and Analysis of the Same.

The method of heating the amide with the acid was the same as in Group I.  
The quantity of acid was made of  
100. cc. of C.P. concentrated hydrochloric acid into a two liter bottle and diluting to a mark on the neck. The same



of about 0.55 N. were obtained. From

the little pieces of wire were measured into each of the three flasks, which were heated at the same time in the same bath. The strength of the acid was found at the time by titrating a portion of the acid solution with standard sodium hydroxide.

With many of the acids represented here, especially those of the alkali series, it was found impracticable to determine the undecomposed acids in the samples as was done with the acids and from nitrobenzenes in the experiments of Group I. Thus, in Group II, it became necessary to find the volume of the sample taken.

To this end a 200 c.c. measuring flask was taken, or set well with



water and then <sup>with</sup> alcohol, ammonia, and  
tried on the finger like the flask was  
measured from a bottle 4.5 cc. of a  
solution containing 0.2% caustic soda  
in each sub-division. A 10 cc. "full"  
pipette was filled to the mark and also  
emptied into the flask, into which the  
sample was blown as the second hand  
of the watch passed the 60 seconds mark.  
The force with which the sample was  
blown in thoroughly mixed it with  
the water and alkali in the flask.  
The 4.5 cc. of caustic soda solution used  
was sufficient to neutralize 5 cc. of  
the reacting solution by mixing with  
the cold water. The temperature was  
immediately brought down to about  
10° C. The flask was put into cold  
water when it was allowed to sit





again the water, being, it has been  
 found in that amount, taken out and  
 filled to the mark with water from a  
 bottle, which the second circulation was filled  
 back down to the same mark. To know ex-  
 actly, the water from the pipette and  
 from the bottle was allowed to flow  
 with a velocity as precise as the same  
 velocity, <sup>each time</sup>  $\wedge$ . The bottle was usually read twice.

The incoming flock was dropped into  
 the proper one of a row of 3000. Under-  
 major flocks and entered twice into the  
 same. As the flock entered the  
 counting machine was started at the  
 same time. This cycle of functions had  
 to be gone through with for each of  
 three flocks every thirty minutes.  
 In the first few runs it was not always  
 possible to get results for a single



at the proper time. In this event the sample was taken several minutes before the actual time recorded.

Each of the measuring flasks were "calibrated" for this special use by drying, measuring in the 4.5 c.c. caustic soda solution and the volume of the 100 c.c. pipette, and filling to the mark from the pipette.

#### Analysis of Samples.

The sample with 10 c.c. of the magnesium sulphate solution was emptied into the distilling flask and washed twice into the same. It was nearly neutralized with caustic soda and finally 2 to 2½ c.c. of a solution of the same, 0.25% in 1 c.c., added. Instead of taking the sample and time to neutralize in acid, the amount of the caustic soda solution necessary to



neutralizing the acid and set free the proper amount of hydrogen as before and was calculated from the known volume of the sample and that amount added, at once, from a burette.

The ammonia was distilled off with steam, and caught in the fumes of standard acid, and titrated as usual.

The amount of standard acid neutralized was divided by the volume of standard acid equivalent to the amide contained originally in the known volume of the sample taken.

In all titrations cochineal was used as indicator. Some solutions made from the same lot of bags worked splendidly while for no known reason others were bad and had to be thrown away. The solutions seem to deteriorate after about ten days.



From about the 4th series on, all of the water used for making up the acid, for putting in the measuring flask etc., and for use when it was being put in the distilling flask, was distilled from sulfuric acid and chromic acid.

The results of the experiments made according to this procedure are given in the following tables.

An amount of each amide equivalent to 4.000g nitrobenzamide was weighed into each flask, except in several cases where the amide was scarce, and in some experiments with difficultly soluble amides where half that concentration was used.





Series 1.

m. Amidobenzamide, p. Amidobenzamide, B.

Conc. of HCl = A = 0.5769 N

Conc. of Amide = B = 0.04026 N.  $A-B=0.5366$ ;  $1/B=14.33$

Dec. 15, 1897.

m. Amidobenzamide,  $C_6H_5\overset{CONH_2}{NH_2} \cdot H_2O$ . 3.712 g.

Time t	Change of Sample	Vol. of Sample	Excess of moles	$\lambda$	A - x	B - x	$\log \frac{A-x}{B-x}$	$\log \frac{A}{B}$
30	62.2	86.1	24.36	28.6	14.07	14.1	.00412	.0172
63	12.78		11.11	4.6	13.64	14.1	.0436	.0172
10	14.38	85.9	24.4	38.6	13.73	14.1	.004161	.0172
120	15.66	80.5	22.61	58.3	13.610	14.1	.004175	.0172
150	13.72	63.1	17.13	78.3	13.33	14.1	.06238	.0172
180	15.10	78.5	22.05	82.1	12.51	14.1	.005009	.0172
210	17.13	68.2	17.1	88.1	13.43	14.1	.0271	.0172
40	13.34	51.4	14.14	11.5	13.42	14.1		

The same concentrations etc. apply to the  
labels found on next page for p. amide-  
benzamide and benzamide. All labels etc.



## p. Amidobenzamide, 3.286

t	Change	Vol of Sample	Eq. of Sample	$\frac{w}{10}$	A	B	$\frac{A}{B}$	$\frac{A}{B} \times \frac{2.282}{3.286}$
30	6.12	81.8	22.97	26.6	14.03	13.4	.00421	.0185
66 $\frac{1}{4}$	10.18	72.0	20.22	50.3	13.55	49.7	.004350	.0187
94	12.61	11.1	12.11	63.4	13.70	36.6	.004432	.0190
120	14.97	16.5	24.2	73.2	13.61	27.0	.004549	.0193
150 $\frac{1}{2}$	18.53	64.0	16.5	81.8	13.51	18.2	.004745	.0204
180	16.50	67.1	12.1	83.6	13.44	11.4	.005035	.0213
210	14.13	70.5	12.1	91.6	13.41	8.1	.005000	.0214
240	—	—	—	—	—	—	—	—

Temperature

Bad.

## Benzamide, 2.917

40	1.41	82.0	23.03	36.5	13.57	63.5	.004654	.0200
61	13.40	81.4	22.17	53.2	13.75	44.3	.004808	.0206
113	14.27	81.7	22.72	68.1	13.67	34.1	.004911	.0211
122	12.72	—	17.1	74.1	13.57	25.7	.004985	.0210
159	16.63	80.4	22.38	84.7	13.50	17.3	.004874	.0209
180	16.44	78.0	21.91	85.1	13.44	11.3	.005106	.0217
211	13.6	—	14.14	92.4	13.41	8.6	.004913	.0211
240	—	—	—	—	—	—	—	—

At. Const.

0.0209



## Series 2.

m. Brombenzamide, p. Brombenzamide, p. Chlorbenzamide.

$$\text{HCl, } A = 0.5538N, B = 0.04026N, A \cdot B = 0.5135, \frac{A}{B} = 13.75$$

$$H. = 1.001110' \quad \dots \quad 39.1.$$

m. Brombenzamide. 4.816g

Dec. 17, 1897

t	Change	Vol. of Sample	Equiv. Sample	% $\lambda$	A x	B x	$\frac{A \cdot B}{A + B} \cdot t$	$\frac{A \cdot B}{A + B} \cdot t$
30	4.11	23.6	20.65	87.3	13.52	56.7	.003546	.0161
60	8.20	47.2	41.22	87.2	13.31	53.5	.003781	.0179
90	10.38	64.2	56.03	87.3	13.13	47.7	.004243	.0190
120	14.38	72.1	60.25	83.6	13.04	41.0	.004288	.0172
150	16.72	74.6	60.56	81.2	12.73	38.2	.004457	.0200
180	19.31	81.1	62.72	77.4	12.70	35.0	.004427	.0177
Av. Count.	210	15.51	73.4	82.2	12.56	32.8	.003708	.0177
0.0184	240	Vol. of Sample lost	-	-	-	-	-	-

Great difficulty was experienced in getting amides in solution. The solubility of the acid formed seems to cause irregularities.



## p. Brombenzamide. 4.816

l	Charged Sample	Vol. Sample	Emp. Sample	% X	A x	B x	$\frac{A \cdot B}{V \cdot E}$	$\frac{A \cdot B}{V \cdot E} \cdot \frac{2.22}{A \cdot B}$
30	3.18	38.1	1.11	20.1	13.54	79.3	.003135	0.0146
60	6.36	36.0	1.21	44.0	13.34	58.7	.003600	.0161
90	10.52	6.7	1.67	53.6	13.21	46.4	.003172	.0181
120	14.67	27.3	2.71	63.1	13.13	39.6	.003438	.0154
150	12.36	63.0	12.71	69.3	13.06	30.1	.003270	.0147
180	13.36	63.1	12.81	74.4	13.11	25.6	.003154	.0141
210	14.32	65.4	18.51	78.6	12.97	22.0	.003011	.0135
240	15.36	62.2	15.53	81.3	12.84	18.7	.002923	.0131

## p. Chlorbenzamide. 3.714g.

30	5.21	74.4	2.040	25.0	13.50	75.0	.003789	0.0170
60	8.11	61.6	15.12	47.7	13.36	55.3	.004047	.0181
90	10.43	63.0	12.70	50.1	13.16	41.1	.004077	.0183
120	14.51	75.2	2.176	63.6	13.08	31.4	.004011	.0180
150	15.10	70.2	15.72	71.1	13.00	24.5	.003910	.0175
180	the gas went away							

As. Count.

210	18.52	73.2	20.52	81.8	12.87	15.1	.004214	.0187
240	14.16	36.1	15.23	88.8	12.86	11.2	.003640	.0172





Series B. HCl.

Dec. 21, 1899.

o.Toluicamide m.Toluicamide p.Toluicamide.

A = 0.5451N. B = 0.04026N. A B = 0.5048.  $\frac{A}{B} = 13.5\%$ .

Bar. 757.4 cm. hence B.P. of water 99.9°C.

o.Toluicamide 3.256g

Standard HCl - 0.1412.

t	Ch. g.	Vol. of Sample	Vol. of Sample	% N	A	B	$\frac{A}{B} \times 100$	$\frac{A}{B} \times 100$
30	0.16	73.7	20.71	3.1	17.50	46.3	.000502	.00229
60	1.30	74.8	21.12	7.1	13.47	42.1	.000445	.00226
90	2.57	91.1	25.39	10.1	13.44	37.7	.000478	.00218
120	2.56	66.6	18.71	13.7	13.40	36.3	.000462	.00211
150	3.30	73.7	20.71	15.7	13.38	34.1	.000467	.00213
180	3.83	70.7	17.73	17.1	13.35	31.6	.000486	.00222
Av. Count.	210	3.73	58.9	16.79	22.2	13.32	.000485	.00221
.00220	240	4.57	67.3	17.47	25.0	13.24	.000487	.00222

Amount of ammonia found in first sample about 1.8 mg.

o.Amides seem to run a little ahead at first or else the analyses are too high, there is ~~so~~ little  $NH_3$  it is hard to say.



## m. Toluicamide 3.256g.

Table 2.303								
t	Charged	Vol. Sample	Equiv Sample	% X	A - x	B - x	$\frac{A \times B}{13 \times 10^6}$	$\frac{A \times B}{13 \times 10^6}$
30	43.8	68.0	19.26	25.4	12.2	74.6	.003777	0.0181
60	5.76	70.1	19.69	74.5	13.10	53.5	.004023	.0183
90	11.81	70.3	19.75	59.5	12.74	40.2	.004179	.0191
120	13.87	70.1	13.89	70.5	12.84	29.5	.004226	.0193
150	14.48	67.8	19.04	78.5	12.75	21.3	.004303	.0196
180	15.71	66.6	18.71	84.1	12.70	15.7	.004382	.0198
210	17.17	68.5	19.24	87.2	12.65	10.8	.004462	.0204
240	3.63	5.7	43.11	91.2	12.62	8.3	.004476	.0200

## p. Toluicamide 3.256g.

30	4.81	71.8	20.17	23.8	13 30	76.2	.003675	(0.0168)
60	7.13	76.3	21.93	42.6	13 11	57.4	.003784	.0173
90	9.32	59.4	16.74	55.7	12 98	44.3	.003725	.0170
120 <sup>12</sup>	12.88	65.4	19.22	67.0	12 87	33.0	.003827	.0175
150	15.93	76.2	21.41	74.4	12 80	25.6	.003782	.0172
180	13.76	58.4	16.41	82.0	12 72	18.0	.003986	.0182
210	15.68	64.5	18.12	86.5	12 68	13.5	.003863	.0176
240	22.18	88.8	24.25	91.3	12 65	8.7	.004272	(.0176)



Series 4.

Jan. 4, 1911.

o-Nitrobenzamide, o-Amidobenzamide, o-Hydroxybenzamide.

$$A = 0.5538 N. \quad B = 0.04026 N. \quad A - B = 0.5135 N. \quad \frac{A}{B} = 13.73$$

Standard  $N/C = 0.1133 N.$ 

o-Nitrobenzamide 4.400 g.

t	Charged	Vol. of Sample.	Eq. Sample	% N	A x	B x	$\frac{A}{B} = \frac{0.5135}{0.04026} = 12.75$	$\frac{A}{B}$	
30	0.22	66.8	18.77	1.2	13.74	98.5	.000164	0.00073	
60	0.42	68.6	17.27	2.2	13.73	97.8	.000150	.00067	
90	0.43	66.1	18.27	2.5	13.72	97.5	.000112	.00050	
120	0.70	67.5	17.52	3.6	13.71	96.4	.000122	.00053	
150	0.99	74.3	20.87	4.7	13.70	95.3	.000129	.00058	
180	1.00	72.3	20.31	4.9	13.70	95.1	.000112	.00050	
Ar. Const.	210	1.16	67.0	18.52	6.2	13.69	93.8	.000123	.00053
0.000574	240	1.66	91.8	25.15	6.5	93.5	.000114	.00051	

The fact that the amount of ammonia found was so very small may account for the irregularity in the first two. 0.22 c.c. = 0.53 mg.  $NH_3$ .  
In this series and the following ammonia free water <sup>was</sup> used.



## o. Amidobenzamide. 3.280.

made. 5.280									
t	Weight of Sample	No. of Sample	Equivalent Sample	$\frac{w}{x}$				$\log \frac{1}{1-B-x} \frac{A}{A-B}$	$\log \frac{2.3026}{A-B}$
30	0.57	58.4	18.65	3.5	13.22	96.5	.000484	(0.00217)	
60	1.20	68.4	18.38	6.2	13.61	92.3	.000432	.00194	
90	1.78	68.8	18.25	8.6	13.66	88.4	.000402	.00180	
120	1.71	68.0	18.85	10.5	13.64	84.5	.000372	.00167	
150	2.40	69.3	18.35	13.4	13.62	81.6	.000389	.00174	
180	3.15	68.1	18.41	16.2	13.58	78.3	.000398	.00178	
210	3.53	67.1	18.02	17.6	13.56	81.4	.000377	.00178	
240	4.71	56.1	24.7	20.5	13.54	77.5	.00035	.00174	

## o. Hydroxybenzamide. 3.328g.

30	1.41	62.5	11.56	8.0	13.67	92.0	.001122	(0.00303)
60	2.63	60.5	11.05	13.7	13.61	86.3	.000992	.00445
90	3.76	66.4	18.22	20.0	13.55	80.0	.001006	.00451
120	4.71	73.4	20.62	23.5	13.51	76.2	.000920	.00413
150	6.15	78.2	18.12	31.4	13.42	68.6	.001025	.00460
180	7.73	77.4	22.30	34.0	13.40	65.2	.000970	.00455
210	11.18	66.0	18.57	38.5	13.36	61.0	.000956	.00424
240	11.44	55.4	20.55	42.4	13.32	57.1	.000936	.00427





Series 3.

HCl.

Jan. 6. 1898.

o-Iodobenzamide. o-Chlorbenzamide. o-Hydroxybenzamide.

A C. 552.3 B C. 552.2 C. 552.1 D C. 552.0 E C. 551.9

Bar. 757.2 mm. Cor. B.P. Water 99.9°C.

o-Iodobenzamide 5.944 - Ammonia 5.944

l	Weight	Vol. of sample	Vol. of sample	Vol. of sample	Vol. of sample	Vol. of sample	Vol. of sample	Vol. of sample	Vol. of sample
60	0.80	67.5	18.96	4.3	13.67	95.5	.000201	.000121	
120	1.34	67.5	18.96	7.1	13.64	92.1	.000263	.00117	
150	1.65	71.6	18.96	8.1	13.63	91.5	.000231	.00112	
180	2.03	71.6	20.03	12.1	13.61	89.9	.000231	.00105	
210	2.27	71.7	19.79	11.5	13.67	86.5	.000234	.00123	
240	2.55	61.6	18.96	13.6	13.67	86.7	.000246	.00111	
Ar. Const.	2.7	73.6	20.03	14.5	13.66	86.5	.000234	.00105	
0.00106	300	79.1	22.22	16.0	13.53	84.0	.000232	.00106	

Here again the first one first and second samples run ahead, but it may be only apparent as the amount of ammonia is very small.



o-Chlorbenzamide 3.744

amide	3.1777							
t	Weight sample	Weight sample	% X	4	11	log	log	
60	1.61	62.6	17.57	46	96.1	.0010697	0.003035	
120	4.12	73.3	20.69	50	96	.001154	.00339	
150	4.0	61.5	17.28	51.1	16.7	.000712	.00320	
180	4.75	68.1	18.51	50.1	72.2	.000708	.00317	
210	5.52	64.1	18.7	52.2	64.7	.000699	.00315	
240	6.31	64.7	18.7	34.7	62.3	.000724	.00326	
270	7.58	70.5	19.81	38.1	61.1	.000726	.00327	
300	11.17	77.3	22.36	40.7	57.1	.000711	.00322	

o-Hydroxybenzamide 3.328

60	2.71	68.4	17.22	14.1	13 37	88.7	.001026	0.00463	
120	4.97	68.4	17.22	25.1	13 45	84.1	.001015	.00455	
150	6.17	73.2	20.66	30.0	13 41	70.0	.000987	.00432	
180	7.75	71.6	22.72	34.1	13 36	65.3	.000966	.00436	
210	7.41	72.51	22.82	32.7	13 32	61.1	.000937	.00432	
240	9.34	71.3	21.11	43.1	13 2	56.6	.000772	.00437	
Av. Const.	2.70	66.9	19.8	41.2	13 24	57.7	.000771	.00440	
0.00437	300	11.59	81.0	22.78	30.7	13 20	47.1	.001115	.00440







p-Nitrobenzamide. 4.00g. 0.2

t	Calor.	Temp.	Sample	...	...	...	...	...	
...	6.11	67.1	...	32.4	12.42	67.6	.00532	0.0238	
60	8.31	68.3	16.65	33.1	12.26	46.1	.005316	.0237	
...	12.31	64.1	11.22	6.1	12.12	32.1	.005239	.0234	
100	13.31	66.1	14.16	21.7	13.02	32.3	.005217	.0233	
120	15.11	64.2	18.52	33.0	12.75	32.0	.005309	.0237	
140	16.41	65.1	15.1	50.0	12.90	30.4	.00524	.0231	
Ar. Const.	15.12	65.1	6.87	93.2	12.57	6.8	.005415	.0242	
0.0236	24	24.61	15.0	28.83	93.1	12.85	4.1	.00532	.0235

Benzamide. 2.917

	5.21	64.6	11.12	28.7	13.51	31.3	.004540	0.0204	
60	7.11	72.7	20.48	48.8	13.32	51.6	.004547	.0203	
	12.05	71.2	13.72	63.6	11.1	36.1	.004648	.0205	
100	14.12	67.1	15.11	72.9	13.01	31.1	.004829	.0202	
120	13.01	68.1	16.1	81.4	12.99	31.6	.004695	.0210	
140	15.14	67.1	13.11	84.6	12.95	31.4	.004360	(.0195)	
Ar. Const.	15.02	68.8	19.90	90.6	12.89	4.1	.004749	.0212	
0.0202	24	14.1	22.3	23.72	73.4	12.87	6.6	.004792	.0217





The samples of *m*. Nitrobenzamide were analysed according to the method in Group I, also, so that the results could be calculated both ways in order to compare the two methods. This shows it better to calculate total amide from volume of sample.

Series 2.

HCl.

Jan. 14, 1898.

*o*. Ethoxybenzamide, *o*. Methoxybenzamide, *o*. Toluicamide.

A = 0.0000 N. B = 0.0411 N. C = 0.1121 N.  $\frac{4}{13} = 0.3077$ .

Bar. = 765.9 mm. cor. B.P. water = 100.2°C. Standard HCl = 0.1433 N.

*o*. Ethoxybenzamide. 2.650g in 40 c.c. of Solution. Material scarce.

1	2	Vol. of Sample	Vol. of Sample	Vol. of Sample	Vol. of Sample	Vol. of Sample	Vol. of Sample	Vol. of Sample
10	5.0	69.3	13.47	26.1	13.47	13.7	.002067	0.00920
120	11.12	12.6	25.27	48.1	12.30	50.3	.002022	.00907
130	11.11	61.5	17.4	57.1	12.15	40.1	.002077	.00941
210	11.68	64.0	17.88	64.7	12.10	40.1	.002077	.00926
240	11.68	64.7	17.88	76.5	12.05	40.1	.002077	.00948
370	11.72	46.4	13.20	78.3	12.17	40.1	.002077	.01060

0.00928



o. Methoxybenzamide, 2.426g. in 500 cc. solution,  $\frac{3}{16}$  usual quan-

*1 liter. as material was little as 100 cc.*

	$t$	Temp.	Temp.	$\lambda$	$\lambda$	$\lambda$	$\log \frac{I_0}{I}$	$\log \frac{I_0}{I}$
	(deg.)		Boiling					
	60	58.0	65.2	13.63	31.1	13.24	63.7	.002531
	120	7.11	52.2	14.66	53.0	13.22	41.0	.002574
	150	11.27	67.0	15.52	62.2	13.13	37.8	.002683
	180	12.22	71.5	20.08	68.3	13.01	31.1	.002648
	210	10.57	54.5	14.87	72.3	12.05	27.7	.002543
Ar. Const.	240	5.72	77.6	24.63	73.7	13.01	26.3	.002316
0.0116	270	21.66	93.0	26.12	80.6	12.77	19.4	.002371

o. Toluicamide, 2.712g in 500 cc. solution uniform with above.

	60	1.36	63.1	11.87	1.6	12.6	92.5	.000527	0.00236
	120	2.44	64.7	11.93	14.1	13.61	83.9	.000573	.00230
	150	3.28	72.1	20.53	16.6	13.55	53.4	.000496	.00220
Previous	180	2.47	64.0	11.92	17.7	13.53	80.1	.000500	.00225
0.00220	210	3.34	64.4	16.46	22.7	13.5	11.4	.000475	.00222
Ar. Const.	240	5.70	78.6	22.05	23.7	13.57	74.1	.000505	.00225
0.00224	270	6.16	83.8	24.98	27.2	13.41	72.1	.000493	.00221



Thin layer should follow page 87.

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p-Chlorobenzamide 3.144

t	Change	Y	X	Y	X	Y	X	Y	X
30	2.52	62.6	5.27	20.1	25.57	62.6	.006079	(0.0221)	
60	2.60	61.1	2.41	45.0	25.70	36.1	.004723	.0205	
90	2.58	57.5	8.74	63.6	25.86	37.0	.005999	.0218	
120	6.15	68.7	2.20	71.2	25.66	36.3	.004663	.0203	
150	8.88	74.2	11.12	76.3	25.37	20.2	.004541	.0197	
180	7.11	67.0	8.23	83.7	25.33	14.1	.004646	.0202	
Av. Const.	210	9.43	74.8	10.60	90.0	25.29	10.0	.004690	.0205
C.0202	240	12.21	10.2	13.00	73.2	25.26	6.8	.005777	.0210

p-Nitrobenzamide 4.000

30	3.87	72.0	10.67	34.2	25.55	60.5	.005870	0.0253	
60	4.14	62.1	8.80	36.1	25.63	42.8	.005802	.0252	
90	7.16	71.8	10.05	71.0	25.46	27.2	.005851	.0254	
120	8.66	76.1	10.68	81.0	25.38	19.0	.005897	.0256	
150	8.14	65.0	9.13	89.2	25.30	10.8	.006344	(.0276)	
180	7.65	60.4	8.48	90.9	25.28	7.1	.005898	.0249	
Av. Const.	210	10.44	71.6	11.54	94.6	25.24	3.4	.005864	.0259
C.0251	240	12.61	72.6	13.00	76.1	25.15	3.0	.006677	.0274



Series S.

HCl.

Jan. 11, 1918.

$$A = 0.5494N. B = 0.02013N. A - B = 0.5293, \frac{A}{B} = 26.19.$$

*p.* Brombenzamide, *p.* Chlorbenzamide, *p.* Nitrobenzamide.

Bar. 769.8 mm. cor. 13.1°, water, 100.35°C.

*p.* Brombenzamide, 2.46 g. 2.5% solution.

<i>t</i>	Change	Vol. of sample	Equiv. of sample	<i>x</i>	<i>A</i>	<i>B</i>	$\log \frac{A-x}{B-x} \cdot \frac{B}{A}$	$\log \frac{2.3026}{A-B}$	
30	2.65	68.8	9.65	27.3	25.42	72.5	.004508	.0111	
60	4.55	65.1	9.70	46.0	25.73	53.8	.004461	.0193	
90	5.65	66.2	9.77	61.1	25.55	45.1	.004442	.0193	
120	7.05	71.3	10.00	70.8	25.48	34.2	.004387	.0189	
Previous	150	8.22	75.3	10.57	77.7	25.41	22.3	.004287	.0185
0.0146	180	8.13	71.3	10.00	81.3	25.38	18.7	.003970	.0172
Av. Const.	210	9.24	76.2	10.69	86.4	25.33	13.6	.004057	.0176
0.0175	240	7.04	58.7	7.82	90.0	25.27	10.0	.014103	.0175

The first two of these had given so much trouble owing to their slight solubility, and the almost insolubility of the acid that half the usual concentrations were tried. This seems to of just the constant, as seen with the *p.* nitrobenzamide.

0.3 cc. on the brom., and 0.2 cc. on others, allowed on vol. of sample for precip.





Series 9.

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Jan. 21, 1876.

p. Brombenzamide, m. Brombenzamide, p. Chlorbenzamide

13. 764.5 mm. c. c. P. P. 10.10 C.

p. Brombenzamide 2.408g 1/2 Usual concentration

t	Change	Vol. of	Equiv. of	%	A-x	B-x	Log(A-x)/B-x	Log(A-x)/B-x
3	2.60	68.6	4.63	27.4				
6	2.30	71.2	4.22	40.7				
9	2.07	69.1	4.66	56.2				
12	6.94	71.7	10.06	67.0				
15	7.37	67.7	4.41	74.3				
18	8.35	74.3	10.43	77.1				
21	7.37	80.1	11.32	82.8				
24		2.11.1						



m. Brombenzamide 2.4084, 1/2 known quantity.

t	Changed	Vol. of Sample	Eqv. of Sample	%	A - x	B - x	$\log \frac{A - x}{B - x}$	$\log \frac{A - x}{B - x}$	$\log \frac{A - x}{B - x}$
30	2.42	70.2	9.86	29.7					
60	4.73	65.4	9.25	29.1					
90	6.00	65.7	9.25	29.9					
120	1.27	73.5	10.32	26.3					
150	3.07	72.8	11.20	22.8					
180	6.15	73.7	12.30	26.2					
210	6.35	71.8	10.00	22.7					
240	11.67	81.4	12.34	24.6					

p. Chlorbenzamide 1.872, 1/2 known quantity.

t	Changed	Vol. of Sample	Eqv. of Sample	%	A - x	B - x	$\log \frac{A - x}{B - x}$	$\log \frac{A - x}{B - x}$	$\log \frac{A - x}{B - x}$
30	2.51	63.5	8.20	27.3					
60	4.25	63.1	8.56	26.0					
90	6.22	71.1	7.75	22.4					
120	3.42	74.5	7.00	22.6					
150	5.77	82.5	11.60	20.1					
180	7.07	62.7	7.25	26.5					
210	3.55	63.7	7.60	22.2					
240	12.60	82.2	11.44	22.6					



Series 10.  $\text{HCl}$ ,  $A = 0$ . $B = 0.04026N$ .  $A \cdot B =$  $\frac{A}{B} =$ 

Bo v. 752.7 g. BP. W. t. 99.73°C.

	t	Changed	Vol. of Sample	Temp. Sample	$\frac{A}{B}$	$\frac{A}{B}$	$\frac{A}{B}$	$\frac{A}{B}$	$\frac{A}{B}$
p. Amido-	2	4.31	64.8	16.61	22.6				
benzamide	6	5.55	11.1	14.47	43.4				
3.250 g.	8	10.11	66.5	18.77	56.4				
	12.0	12.12	63.9	16.91	66.7				
	15.0	16.25	15.5	26.31	76.8				
	18.0	19.25	66.2	16.60	82.6				
	21.0	14.02	57.6	16.15	86.1				
	24.0	26.71	33.0	23.31	123.5				
m. Amido-	20	4.31	67.1	12.51	24.1				
benzamide.	6	5.55	70.6	15.54	42.4				
3.715 g.	8	10.27	65.1	18.27	56.3				
	12.0	—	Running out.						
	15.0	16.28	61.3	18.17	73.8				
	18.0	16.66	32.7	26.76	85.3				
	21.0	16.41	72.1	20.25	86.1				
	24.0	—	Running out.						



## Recapitulation.

			<i>o</i> -Amide-	<i>o</i> -Chlor-	<i>o</i> -Iodo-	<i>o</i> -Nitro-
Group	Weight	Retention %	0.00217	0.00305	0.00130	0.00073
-CH <sub>3</sub>	15	0.0187 59.4	.00194	.00339	.00119	.00067
-NH <sub>2</sub>	16	0.0191 91.5	.00180	.00320	.00104	.00050
-OH	17	0.0165 79.1	.00167	.00317	.00108	.00055
-OCH <sub>3</sub>	31	0.0093 44.1	.00174	.00315	.00105	.00058
-Cl	35.4	0.0177 84.6	.00178	.00326	.00111	.00050
-C <sub>2</sub> H <sub>5</sub>	45	0.0116 58.8	.00173	.00327	.00105	.00055
-NO <sub>2</sub>	46	0.0204 97.1	.00174	.00322	.00106	.00054
I	121	0.0198 94.9	0.00178	0.00321	0.00106	0.00054

<i>o</i> -Toluic-	<i>o</i> -Toluic	<i>o</i> -Hydroxy-	<i>o</i> -Hydroxy	<i>o</i> -Methoxy-	<i>o</i> -Ethoxy-
0.00229	0.00236	0.00303	0.00463	0.0114	0.0092
.00226	.00230	.00445	.00458	.0115	.0091
.00218	.00220	.00451	.00432	.0120	.0094
.00211	.00224	.00413	.00436	.0119	.0093
.00213	.00222	.00460	.00433	.0114	.0095
.00222	.00228	.00435	.00434	(.0104)	(.0160)
.00221	.00221	.00429	.00440	.0116	
.00222		.00429	.00440		
0.00220	0.00224	0.00437	0.00437	0.0116.	0.0093





## Summary of Constants.

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Benzamide	Benzamide	m. Nitro -	p. Nitro	$\frac{1}{2}$ conc. p. Nitro	m. Amide	p. Amide
0.0200	0.0207	0.0197	0.0238	0.0235	0.0172	0.0180
206	203	197	237	232	178	187
211	205	198	234	234	179	190
200	202	194	233	236	176	193
209	210	194	237	(276)	184	204
219	(195)	198	234	248	172	218
211	212	197	242	238	183	214
	214	198	235	(279)	191	—
0.0209	0.0208	0.0196	0.0236	0.0236	0.0177	

p. Chlor -	$\frac{1}{2}$ conc. p. Chlor -	m. Brom -	p. Brom -	$\frac{1}{2}$ conc. p. Brom -	m. Toluic -	p. Toluic -
0.0170	(0.0221)	0.0161	0.0140	0.0196	0.0181	0.0168
181	205	179	161	193	183	173
183	208	190	157	193	191	170
180	203	192	154	189	193	175
175	197	200	147	185	196	172
	202	199	141	172	195	182
187	204	177	135	176	204	176
172	204		131	178	200	(186)
0.0179	0.0204	0.0184		0.0186	0.0193	0.0175



## Discussion of Results.

Experiment, Temp. 1.

Series 1, 2, 3 & 4 with hydrochloric acid show very clearly that o-nitrobenzamide reacts extremely slowly to the action of the acid while the nitrate is readily hydrolyzed and the form still more so. The constants obtained for the nitrate and form do not vary specially with different concentrations of the acid. The variation in the constant found may be due to change of barometric pressure. As a very dilute acid is much more completely dissociated it would be expected to give a higher constant. The ammonium salt formed certainly retards the reaction, comparatively, much more with a weak than a strong acid. These two opposite effects may balance and keep the actual velocity very nearly the same.



Series 5, 6 & 7, indicate that the relations between the rate of formation of the products are approximately the same with sulphuric acid as with hydrochloric acid. The results, though not quite comparable show that the sulphuric acid is about 0.45 times as strong as hydrochloric. Should one wish to compare the strength of acids by measuring the rates at which they hydrolyze a given amide it seems that it would be proper to divide the average constant found in a series with one by the similar average constant found with the other, the conditions under which the measurements were made being the same. Some of our results are in the abstract tables in the *Hydrolysis of acetonitrile, acetylacetone, and propionitrile*, published the strength of various acids, estimated the strength of various acids.

I. ph. Ch. 111 112, 113.



acids from the times it took them to hydrolyze 5.00 g of the acid anhydride.

### Experiment Group II.

In series 1, the caustic soda was made by adding sodium to water. The results show a high but decreasing constant. In series 2, the alkali was made by adding barium hydroxide to an approximately 1% solution of pure sodium sulphate. The large excess of sodium sulphate seems to have retarded the reaction. The slowing up of the reaction due to formation of neutral salt in addition to that already in solution appears also in series 3 and 4. In the later the meta does not seem to have gone into solution quickly. In series 5, neither seems to have started promptly, which gives to the reaction the appearance of acceleration. Sometimes it is difficult to induce substances to dissolve





as quickly as is desirable for such work even though more than enough of the solvent is present. Series 6 gave a good constant for the meter. The pairs could not be trusted to dissolve sufficiently at this temperature. The few determinations here made with benzene do not warrant any conclusion.

Series 8 is with caustic potash, which was likewise prepared from potassium sulphate and barium hydroxide, practically duplicate the corresponding one with caustic soda. In Series 8, it was known that the meter did not dissolve quickly which accounts for the low value of the constant at first.

Series 10 and 11 with barium hydroxide gave much higher constants than those with either caustic soda or potash. This is attributable to the absence of the neutral



salt. The salt which was found in the reaction at the end of the experiment. The great influence of the reaction salt was not realized until these experiments were made, otherwise the excess of sodium and potassium sulphates in the previous series would have been avoided.

### Influence of Temperature.

The presence of sodium sulphate in the experiments with caustic soda deprive the results of much of their value, but as about the same amount was found in each case some conclusions may be drawn as to the relative velocities at different temperatures. In conducting these the average results found were

at	60°	70°	80°	90°	100°C.
----	-----	-----	-----	-----	--------

0.038	0.101	0.187	0.305	0.485
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These values were found and the



constants for intermediate degrees estimated from the curve. When this series of values was examined its members were found to be very nearly in geometrical progression. The geometric mean of the calculated values was  $0.37$  and  $0.47$  extremes. The two are here given

60° 70° 80° 90° 100°

0.058 0.107 0.184 0.305 0.485 Experiment.

0.058 0.097 0.168 0.285 0.485 Calculated.

The agreement is as close as could be expected considering the known amount of the constant. Such a comparison would make it easy to compare results obtained at temperatures not too far apart, such, for instance, as the temperatures of boiling water in barometer observations. It is intended to make and use such a comparison for obtaining constants



conditions" the result of the reaction is  
 fragments of temp. etc.

Witt Hoff and others have shown that  
 the variation of the constant for low  
 pressure should be of the form

$$k = \frac{A}{T^2} + B.$$

where  $T$  is absolute

temperature and  $A$  and  $B$  are quantities  
 depending on the nature of the reaction.

Bathford has shown in esterification  
 experiments that in this expression  $A$   
 may be 0 when it takes the form  $k = abT$ ,  
 which agrees exactly with the conclusion  
 reached above.

The few experiments made with benzamide  
 show that it resists hydrolysis  
 by caustic soda about as well  
 as it resists the influence of acid.





## Experiments Nos. I-III.

The experiments with the various unites studied were made under as nearly the same conditions as convenient so that the results would be more directly comparable. The earlier results are, of course, not quite so good as those obtained later. It is regretted that in many instances mistakes were which are out of harmony with the agreement. These are due to various causes, sometimes to mistakes in measuring the samples, or in sealing bottles, and sometimes to causes unknown. In making up the group results, the liberty was taken of throwing out figures evidently erratic. p. l. m. l. h. g. unites has so far failed to give satisfactory results. It was hard to get the distillate to come over neutral



and there seems to be something which interferes with the end reaction in titrating.  $\text{pH} 10$  and  $\text{pH} 11$  being similar were used in solution slowly and as the corresponding acids were formed they were titrated at once at  $\text{pH} 10$ , and seemed to bring down some of the results with them. This led to several series in which half quantities were used. These gave much higher and, in general, better results but the analytical difficulties were much increased as 100% decomposition was only 20 mg. ammonia in many cases. Even 1% of this amount is rather a small amount of ammonia. The results obtained in a similar series with  $\text{pH} 10$  and  $\text{pH} 11$  were about 4% higher than those at the ordinary concentration even after allowing for the unusually high  $\text{pH}$  results.



The cause of this is not yet known.

The possibilities of the method may be judged from the comparison of the results for benzamide in run 6, according to the new method, in which the total variation is only 2% of the value of the constant.

This variation in the constant may be accounted for by an error of several tenths of a percent in the analyses.

### Conclusions. x

The results obtained with the substituted benzamides go to show that groups in this position usually exercise some, though not very marked retarding influence on the rate of hydrolysis. The rate does not seem to vary inversely as the molecular weight as Kellas <sup>\*</sup> concludes in the case of the aliphatic

\* Kellas. *Ann. f. phys. Chem.* 1897 p.



of meta-substituted benzoic acids. The nitro group in the para position causes a very marked increase in the speed of the hydrolysis.

The experiments with other substituted benzoic acids all show that groups in this position exercise a considerable "protective" influence on the amide group. With similar groups this influence varies roughly with the weight of the group, but otherwise it seems to depend more on the nature than <sup>the</sup> weight of the group. For instance methyl with a weight of 15 "protects" better than chlorine, or even  $-OCH_3$ . The nitro group is very remarkable in its protective power for though it has a weight of 46 it "protects" more than twice as much as 126. The methoxy- and ethoxy groups are





remembers for their slight influence, for less than that of hydroc. <sup>104</sup>

The general results of the work of Kellas, Schenck, Kellner, and others on the rates of formation of ethereal salts are generally in harmony with those here found, except that in the formation of ethereal salts the weight of the group seems to be of far more importance than its nature.

Kellas found the nitro group in the nitro function to be in exceptional retarding form. The two lines of investigation seem entirely analogous and the results when more than ought marked out will be interesting to compare. The study of the hydroc. series seems to have many advantages over the other line. The experiments are so much simpler, the reactions are better understood, and the



generally free from complications. The reaction does not take place at such low temperatures as does the formation of other salts. The possibility of using such reactions is a small advantage.

The greatest advantage is a simple and direct method of analysis.

It is hoped to extend this work further and especially to take up the hydrolyses of these amides with alkali.

A large part of the results <sup>above</sup> ~~herein~~ given are brought together graphically in ~~curves attached~~.



## Biographical

The author of the foregoing dissertation was born at Pinckney, Virginia, June 27, 1872.

Excepting two months at school his early education was in the hands of his parents until he entered Homestead Academy, Chesterfield Co. Va. in January 1886.

From the academy he entered Richmond College, September 1888. He remained there until he received the degree of Master of Arts in 1892. The two years following he taught science and French in Northern College, Louisiana.

In 1894 he entered the Johns Hopkins University where he has since been engaged in the study of Chemistry with physics and mathematics as subordinates. In 1894 he was appointed Hopkins scholar which position he held for two years.



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In 1860 he was awarded a prize of one  
thousand dollars for an essay on "The  
Relation of Chemistry and Photography".  
In 1861 he was appointed Lecturer of  
Physics. During the same year he  
served as Demonstrator of Chemistry at  
the University of Maryland.

In the Spring of 1861 he received the  
appointment of Fellow for the present  
year.































































**FOLD OUT**

$\text{c.OCH}_3$   
 $\text{c.OC}_2\text{H}_5$

$\text{c.OH}$

$\text{c.Cl}$

$\text{c.CH}_3$

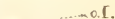
$\text{c.I}$

$\text{c.Br}$



**FOLD OUT**

side.  
(3)



2'

2 1/2 30'



# Various Amides with HCl 1/2

